ABSTRACT

Title of thesis: IMPROVEMENTS TO REFRIGERANT FLAMMABILITY TESTING THROUGH USE OF A POLYCARBONATE APPARATUS

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There is a new generation of mildly flammable refrigerants that pose unique challenges to flammability limit testing with ASTM E681. This test standard relies on visual observation of flame propagation inside of a spherical glass vessel. The combustion of these refrigerants etches the glass test vessel, making it difficult to properly observe the flame. The current standard specifies the electrodes to be placed vertically in the flame path, hindering the propagation of the flame. The rubber stopper that seals the vessel is prone to leak and also vent before the flame fully propagates, skewing the results of the test. These problems have been addressed through the creation of a polycarbonate testing apparatus that utilizes a weighted rubber stopper and electrodes that penetrate through the side of the vessel. This prototype was tested extensively with R-32, and yield a lower flammability limit of 14.8% when testing with a starting pressure of 91.2 kPa. The polycarbonate prototype proved to be an adequate alternative to the glass flask, and provided solutions to the etching, quenching, and venting issues.

IMPROVEMENTS TO REFRIGERANT FLAMMABILITY TESTING THROUGH USE OF A POLYCARBONATE APPARATUS

by

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Chapter 1: Introduction

1.1 Background

A new generation of refrigerants has emerged because of their minimal effect on the ozone layer and low global warming potential. These refrigerants are mildly flammable and have warranted a new flammability classification known as A2L. This classification means that they meet the specifications of A2 (lower flammability) and also have a burning velocity $\leq$10 cm/s while tested at 23 °C and 101.3 kPa [5].

ASHRAE 34 [5], The Designation and Safety Classification of Refrigerants, is a standard that utilizes ASTM E681 to determine the flammability of refrigerants. ASTM E681 is the Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases) and utilizes a visual observation of flame propagation inside of a spherical glass vessel to determine flammability limits. After a vacuum in the sphere is reached, the desired fuel/air mixture is introduced via partial pressure method, and then mixed and ignited with a spark. To consider the mixture flammable, the test standard requires the flame to propagate upward and outward 90° from the ignition point when the flame reaches the wall of the flask, or at least is within 13 mm of the wall [1]. ASTM E681 allows for either a 5 L or 12 L spherical flask to be used but ASHRAE 34 requires the 12 L flask to be used to

eliminate quenching from the flask walls [5]. A picture of the apparatus from ASTM E681 is shown in Figure 1.1.

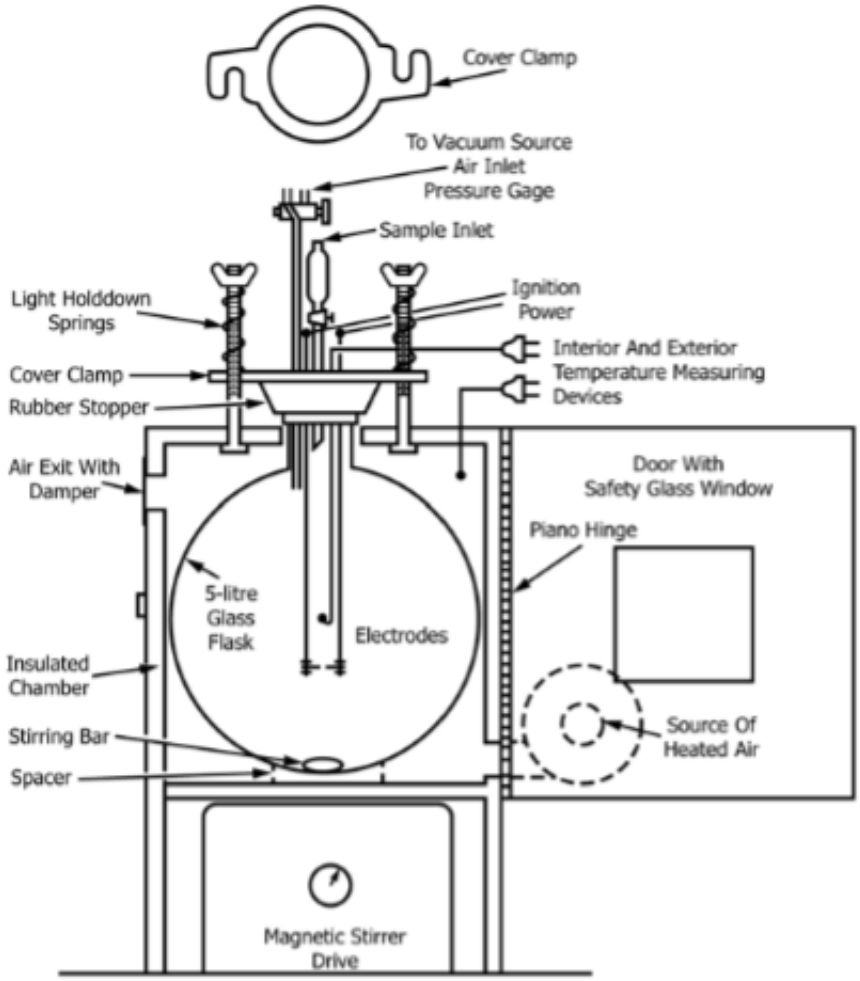


Figure 1.1: ASTM E681 apparatus, with 5L flask as shown in test standard [1].

This thesis is part of a combined effort by current and past students at the Univsersity of Maryland to analyze the current test method for determining flammability limits of refrigerants and suggest improvements to the standard. The initial phase of this project included work done by Conor McCoy and Peter Lomax. Their work is summarized below. Concurrent work done by Alexandra Klieger is also summarized below.

1.1.1 Work Done by Lomax

Lomax developed a fully functioning ASTM E681 testing apparatus at the University of Maryland [3]. Each step in the creation of the apparatus was discussed in detail and several changes to the standard were proposed. Several components of the apparatus include the suggested changes that were made about the standard. One notable change was an altered plumbing system that allowed for continual monitoring of pressure in the flask while also minimizing the penetrations and leakage paths into the apparatus. Also, 3D printing was utilized to make fully functioning components of the ignition system and stirring system that were not easily accessible for purchase. A full control panel was built which allowed for easy control of the high powered spark ignition system and also created a user-friendly interface for controlling the plumbing and constantly monitoring the pressure in the flask [3].

1.1.2 Work Done by McCoy

McCoy conducted an extensive literature review on the topic of refrigerant flammability [4]. Also included in his work was interview results with a number of experts who currently conduct the ASTM E681 test. Many of them expressed concerns with inconsistent venting of the rubber stopper which led to the motivation for an alternative. Instead of a rubber stopper for venting, a burst disc was developed in an attempt to create more consistent testing conditions between laboratories and to also ensure that the test vents after the flame fully propagates to the wall. The burst disc utilized a foil sheet secured over the top of the flask and a knife edge

that punctured the foil when the pressure rose inside the vessel [4]. The burst disc proved to be an acceptable alternative to the rubber stopper, but was not used in this thesis.

1.1.3 Work Done by Klieger

Klieger [6] conducted extensive research on pressure rise in the flask during testing. The goal was to find a suitable pressure rise criteria to represent the lower flammability limit instead of relying on visual observation of the flame propagation. A high frequency pressure transducer was used with a data acquisition system to measure the pressure during the flame event. Klieger's work was done in conjunction with this thesis. The pressure measurements aided in the development of the polycarbonate prototype, especially when characterizing the venting phenomenon.

1.2 Objectives

The focus of this research is addressing inherent flaws of the ASTM E681 test standard that have previously not been addressed. The first issue is the etching of the glass that occurs because of the products of combustion from testing various refrigerants. The etching affects the transparency of the glass flask and makes for difficult flame propagation analysis. The second issue is the possible quenching of the flames due to the electrode rods that are located directly in the flame path.

A literature review was conducted to investigate both of these issues and aid the development of a possible solution. Next, a polycarbonate test vessel was created

as an alternative to the glass flask used previously. The polycarbonate vessel was tested extensively to determine if it is an acceptable alternative to the glass flask. After comparison to results from previous work in the glass flask done by Lomax and McCoy, the effects of the electrodes were quantified based on their influence on flame angle. Finally, the venting issue that was investigated by McCoy [4] was addressed in the form of a weighted rubber stopper. The performance of this stopper was analyzed to ensure that the test could be performed at atmospheric pressure with no leakage, and that the stopper did not vent until after the flame propagates to the vessel walls.

1.3 Literature Review

This literature review is focused on gaining insight applicable to the research goals of this thesis. The topics covered include quenching of refrigerant flames, etching of glass from hydrogen fluoride (HF), and various characteristics of polycarbonate and PVC in order to assess their adequacy as an alternative apparatus for ASTM E681.

1.3.1 Quenching of Mildly Flammable Refrigerants

K. Takizawa et al. [7] conducted quenching distance measurements of mildly to highly flammable compounds to better understand the minimum ignition energies and quenching characteristics of compounds with low-global warming potential (GWP). They used varying sized parallel plates with a spark ignition source to analyze the quenching distance of different compounds in both a vertical and horizontal

orientation. The quenching distance was defined as the minimum distance between two surfaces that allowed for self-sustained propagation of a flame. Both orientations were used because the slowly propagating flames created by mildly flammable compounds are significantly affected by buoyancy. The experimental results from this study showed a quenching distance for R-32 of 7.55 mm in the horizontal plate orientation and 6.45 mm in the vertical plate orientation. These values are significantly larger than the quenching distances for propane, which were only 1.70 mm in both horizontal and vertical orientations [7].

This report also reviewed the quenching effect of the electrodes. It concluded that ignition should be made with an electrode gap that is wider than the quenching distance of the fuel or the flame heat loss to the electrodes could significantly impact the flame propagation. This could lead to a larger reported minimum ignition energy as well as an inaccurate value for the lower flammability limit [7].

I. Kul et al. [8] conducted flammability limit measurements per ASTM E681 to analyze the effects of vessel size. They conducted tests with R-32 at 21°C in 3, 5, 12, and 20 L vessels. They focused on addressing the impact of quenching from the vessel walls, which is why the 3 L flask was included even though it is not incorporated as an option in the ASTM E681 method. The lower flammability limit for R-32 from the 3 L flask was about 8.5% greater than the LFL from the larger flasks. As the vessel size was increased, the effect on lower flammability limit decreased significantly, with a 1.8% higher LFL in 5 L compared to 12 L, and a 0.95% higher LFL in 12 L compared to 20 L. It was concluded that quenching effects were minimized and almost negligible in vessels 5 L or larger [8].

R. Richard [9] conducted flammability limit tests for two different refrigerant blends in a 5, 12, and 200 L vessel in order to compare current small scale testing methods to true ignition and flame propagation in free space. It was emphasized that the most conservative situation for analyzing flame propagation was one where the propagation was completely unhindered and all the energy from combustion is used to propagate the reaction. Richard stated that the low combustibility of many refrigerants led to hindered observations of flames due to significant heat losses to the walls of the 5 and 12 L vessels. Testing in the three vessels revealed that the 90° flame propagation criteria used in the 12 L vessel of ASTM E681 corresponded well to full propagation in the 200 L vessel [9].

1.3.2 Etching of Glass from HF

M. Ito et al. [10] conducted a study to assess the risks of when low-GWP refrigerants are exposed to high temperatures and begin to decompose. In this study, refrigerant/air mixtures were exposed to a heated tube and the resulting refrigerant and HF concentrations were measured. From the tests with R-32, the results show a dramatic decrease in R-32 concentration and a large increase in HF concentration when the heater temperature was approximately 570-590 °C. The production of HF from the thermal decomposition of R-32 is [10]:

$$CH_2F_2 + O_2 \longrightarrow 2\,HF + CO_2 \tag{1.1}$$

G. Spierings [2] conducted a review of wet chemical etching of silicate glasses

in hydrofluoric acid (aqueous form of hydrogen fluoride) based solutions. The glass flask that is used in the ASTM E681 apparatus is composed of 80.6% SiO_2 [11]. The etching process of glass is of high interest in many technological fields. The etching process of silicate glass is described with the following chemical equation [2]:

$$SiO_2 + 6\,HF \longrightarrow H_2SiF_6 + 2\,H_2O \tag{1.2}$$

One major effect of this etching process on glass is the removal of surface material. The glass also experiences changes in surface morphology as the originally smooth surface is roughened and cusp-like structures are formed. Figure 1.2 depicts the transformation of a glass surface with minimal flaws due to wet chemical etching, where (a) is the initial surface, (b) is after etching 0.2 time units, (c) is after etching 1 time unit, and (d) is after etching 3 time units. The dashed line represents the glass surface [2].

1.3.3 Use of Polycarbonate in Testing Apparatuses

A review of the literature found little to no previous work on flammability testing using a polycarbonate vessel. However, several cases of research with explosive conditions have utilized polycarbonate viewing windows, suggesting the functionality of polycarbonate in a high temperature and high pressure environment.

S. Miller [12] conducted a study on the relationship between a pre-detonator and the detonation channel of both a Pulse Detonation Engine (PDE) and a Rotating Detonation Engine (RDE). The testing setup used a center steel plate and

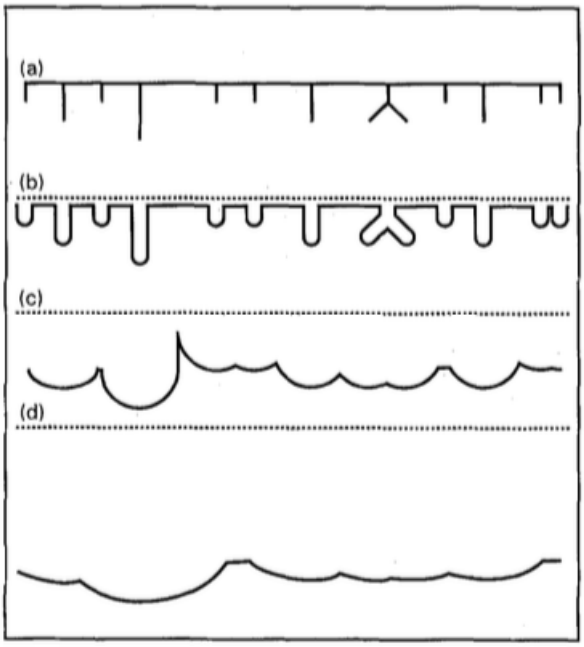


Figure 1.2: Transformation of a surface with closed microcracks or flaws into a cusp-like glass surface by wet chemical etching [2].

two surrounding polycarbonate viewing windows housed by steel framing. The center steel plate and polycarbonate windows created a 6.35 mm channel where the hydrogen/oxygen mixture was ignited and the transition from deflagration to detonation was observed. The polycarbonate windows in this test setup were 12.7 mm thick [12].

R. Boring et al. [13] conducted an equivalency review and comparison between the Mine Safety and Health Administration (MSHA) and the International Electrotechnical Commission (IEC) Explosion-proof Enclosure Standards. This report stresses that the only non-metallic materials that may be used for any viewing ports in explosion-proof enclosures are glass and polycarbonate. This report also specifies that the normal operating interior temperature of enclosures with glass or polycarbonate windows is 115 °C. These explosion-proof enclosures must also with-

stand a minimum of 150 psig (1034 kPa) without leakage through any port that would compromise its integrity [13].

Nalgene Corp. manufactures a 4.7 L vacuum chamber made of clear polycarbonate. This product is advertised to be used as a controlled environment for degassing operations and freeze drying. This chamber is not specified for any flame testing, but does show that clear polycarbonate can be a reliable material to hold a vacuum. The nominal thickness of this chamber is 3.81 mm [14].

1.3.4 Thermal Degradation and Flammability of Polycarbonate and PVC

M. Hirschler and A. Morgan [15] compiled thermal decomposition data for several polymers. It was reported that the glass transition temperature for polycarbonate is 145 - 150 °C, and for PVC it is 80 - 85 °C. The crystalline melting temperature was reported as 215 - 230 °C for polycarbonate and 75 - 105 °C for PVC. The glass transition temperature is typically the limiting temperature for use of a polymer. This data included the minimum thermal decomposition temperature gathered from a 10-mg sample exposed to a 10-K/min heating rate in a nitrogen atmosphere. It was reported that the minimum thermal decomposition temperature for polyvinyl chloride (PVC) was 83 °C [15].

B. Jang and C. Wilkie [16] studied the thermal degradation of bisphenol A polycarbonate in air compared to its degradation in nitrogen. It was found that mass loss in air begins at 450 °C, which was 50 °C earlier than in nitrogen. They concluded

that the degradation in air occurred slightly earlier because oxygen mainly affects the surface of degrading polymers. However, this early reaction of the degrading surface with the air creates an intermediate char on the surface that makes the mass loss in air slower than that in nitrogen [16].

A. Mensch et al. [17] completed a study on fire exposures of fire fighter self-contained breathing apparatus (SCBA) face piece lenses. The lenses that were tested were made of 2-3 mm thick clear polycarbonate. The reports explains that polycarbonate has been used for SCBA lenses because of its thermal resistance, impact resistance, and optical clarity. The testing aimed to simulate different house fire exposures with varying temperatures and heat fluxes. The heat fluxes ranged as high as 20 - 50 kW/m^2, and ceiling temperatures reached as high as 500 - 750 °C. Heat flux gauges and thermocouples were places on the lenses to monitor their exposure throughout the tests. It was found that in all cases, once polycarbonate reached its glass transition temperature, the polycarbonate began to lose its integrity and became vulnerable to physical impact [17].

A. Morgan and M. Bundy [18] conducted cone calorimeter analysis of several UL-94 V-rated plastics. This report summarized the UL-94 ratings of the various plastics and also showed the results from exposures to various heat fluxes in the cone. The harshest conditions tested in the cone were 3.2 mm thick samples exposed to 90 kW/m^2. The information of most interest for this research is the time to ignition after exposure to the heat flux. The clear polycarbonate sample, which has a UL-94 rating of V-2, took 40 s until ignition. The PVC sample, which has a UL-94 rating of V-0, took 11 s until ignition [18]. This data was not gathered for direct comparison

of how these plastics would perform in this research project, but was used for a general understanding of how these plastics behave when exposed to harsh heat fluxes.

1.3.5 Literature Review Summary

One problem with the flammability testing of refrigerants in the ASTM E681 apparatus is the etching of the glass flask. The HF produced from combustion creates a surface reaction on the flask wall and causes a significant change in structure and transparency. Polycarbonate is a transparent plastic that is shown to withstand heat very well, and is being considered for use in the flammability testing. It has been used for viewing windows in explosive environments, showing it has the ability to withstand high heat and pressure. Both polycarbonate and PVC have relatively high thermal degradation and glass transition temperatures that are above 60 °C (elevated testing temperature specified by ASHRAE 34 [5]). When exposed to harsh heat flux conditions, both plastics last a relatively long time (with respect to flames in ASTM E681) before any ignition occurs. This research will attempt to utilize these benefits of polycarbonate to create a solution to the glass etching problem.

There is an abundant amount of literature that identifies 2L flammable refrigerants as being highly affected by quenching due to the test apparatus. There is evidence showing that the electrode spacing has an immediate effect on the propagation of the flame. Also, there is sufficient experimentation on the quenching effects from the vessel walls. This drove ASTM E681 to include a 12 L flask option for fuels

that have large quenching distances. However, no significant literature was found that addresses the quenching effects of the electrode rods that are placed directly in the center of the flame path. The orientation and structure of the glass flask complicates the positioning of the electrode rods, restricting them to the opening at the top of the flask. One goal of this research is to quantify the effects of the electrode rods on the flame propagation angle and also provide a solution for the quenching effects.

Chapter 2: Experimental Apparatus

2.1 Polycarbonate Flask

ASTM E681 calls for a 5 L or 12 L spherical flask to use as the testing vessel. To minimize wall-quenching effects [1], the 12 L glass flask was used in the original apparatus at the University of Maryland [3]. All previous refrigerant flammability limit testing with ASTM E681 has used a glass flask, which is prone to significant etching and loss of transparency due to the surface reaction with HF. A possible alternative to the glass flask is to use a clear polycarbonate flask with the possibility that no loss of transparency will occur following the combustion of refrigerants. When first attempting to find a polycarbonate alternative, custom plastic manufacturers were contacted to request a quote for a clear polycarbonate flask nearly identical to the glass flask that was being used. The majority of custom plastic manufacturers replied and stated that this type of part would need to be blow molded, and due to the low quantity of flasks needed, no one was willing to create the mold for the polycarbonate flask. The next option was to construct a flask using a readily manufactured polycarbonate sphere and attach a separate neck.

The need for a clear polycarbonate sphere led the search to lighting globes designed for outdoor streetlights. There are several manufacturers of clear polycar-

bonate spheres that are available off the shelf at a moderate price ($45.00) [19]. The available option that was closest in dimensions to the glass flask was a 30.5 cm (12 in.) diameter sphere, with a 10.8 cm (4.25 in.) opening at one end. The volume of this sphere was (with neck attachment) 13.9 L. This was slightly larger than the glass flask, which had an actual volume of 12.4 L. The thickness of the polycarbonate spheres ranged from 3.18-6.35 mm (0.125-0.25 in.). The diameter of the glass flask was 29.5 cm, with a thickness ranging from 2-7.6 mm. It was determined that having a slightly larger flask would have no negative effects on the test results [8,9]. A picture of the standard glass flask and the new polycarbonate sphere is shown in Figure 2.1.

(a) Glass Flask (b) Polycarbonate Sphere

Figure 2.1: Pyrex® 12 L glass flask and 30.5 cm diameter polycarbonate sphere.

The clear polycarbonate lighting globe is constucted of Lexan Resin 203, a product of GE Plastics. The Lexan Polycarbonate was evaluated for chemical com-

patibility via GE's test method. The test involves exposing samples to the chemical under defined temperature and stress conditions for a seven day time period. For exposure to 25% Hydrogen Fluoride, the Lexan Polycarbonate reacted "good". GE defines good as "found unaffected in its performance when exposed with regards to time, temperature and stress according to the GE-test method" [20].

2.2 PVC Neck

To allow for testing in the polycarbonate sphere, a PVC neck was connected to the 10.8 cm opening. The goal when creating the attached neck was to make the polycarbonate apparatus equal in dimensions to the glass flask. A 15.2x15.2x1.3 cm (6x6x0.5 in.) PVC sheet was glued to the top of the polycarbonate sphere, and then the 15.2 cm (6 in.) long, 5.25 cm (2.067 in.) internal diameter (I.D.) Type 1 PVC pipe was glued to the PVC sheet. The 5.25 cm diameter PVC pipe allows for a size 14 rubber stopper to be used for venting, as prescribed in ASTM E681 [1]. The glue used was industrial grade silicone sealant [21]. In addition to the hole drilled in the PVC sheet for the neck attachment, a hole for the plumbing connection was also drilled and tapped. The neck on the glass flask was approximately 5.46 cm I.D. and 9.47 cm long. The PVC neck that was attached to the polycarbonate sphere was several centimeters longer than the neck on the glass flask, but the additional height conveniently allowed for the plumbing tree to operate without interfering with the rubber stopper. A diagram of the PVC neck is shown in Figure 2.2. A picture of the PVC neck glued to the polycarbonate sphere is shown in Figure 2.3.

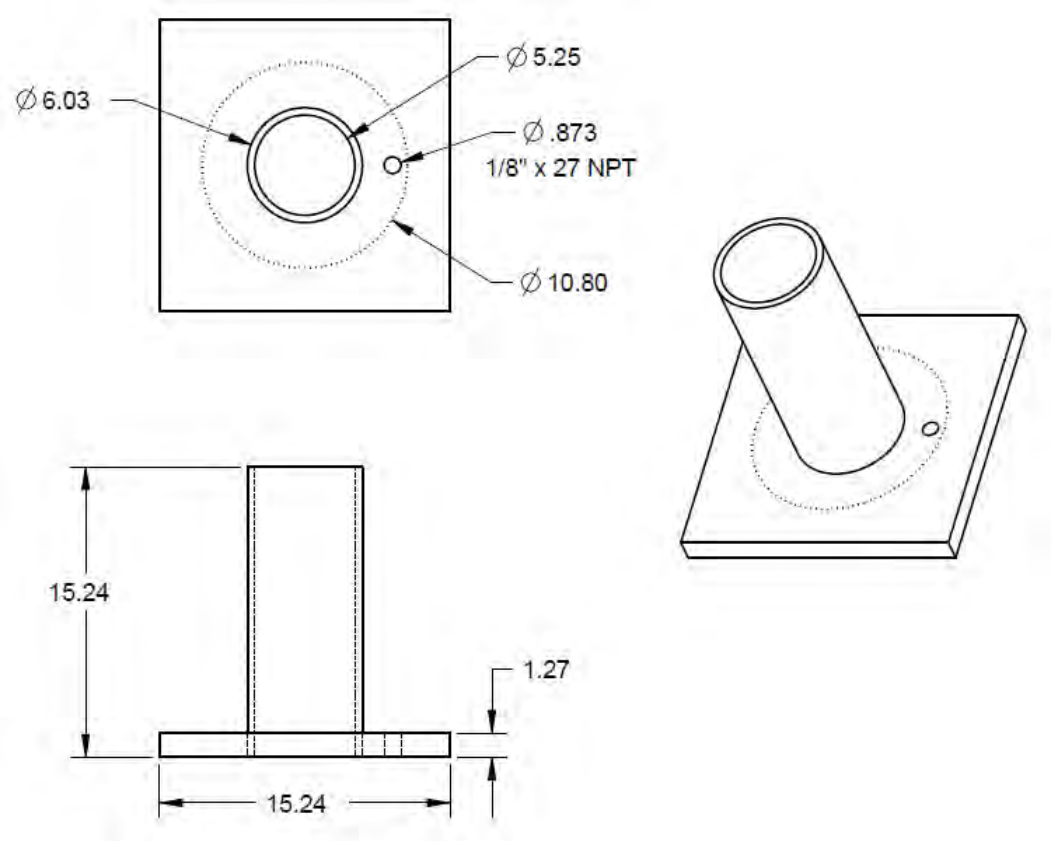


Figure 2.2: Drawing of the PVC neck. All dimensions are in cm, with exception of thread classification (in.). The dotted circle represents the opening of the polycarbonate sphere.

The PVC neck was made with schedule 40 PVC pipe, and the sheet was made with schedule 80 PVC. IPEX, a large supplier of non-metallic pipe and fittings, produced a chemical resistance guide for PVC. The results in the guide were gained from short-term immersion of unstressed PVC in each chemical. For immersion in hydrogen fluoride (undiluted), PVC received an "N" for "not resistant" [22]. The actual exposure concentration of PVC to HF in this research is unknown, and expected to be much less than the undiluted immersion from the report. PVC was still used for the construction of the neck of the flask, but a polycarbonate tube (if available) would have better resistance to HF.

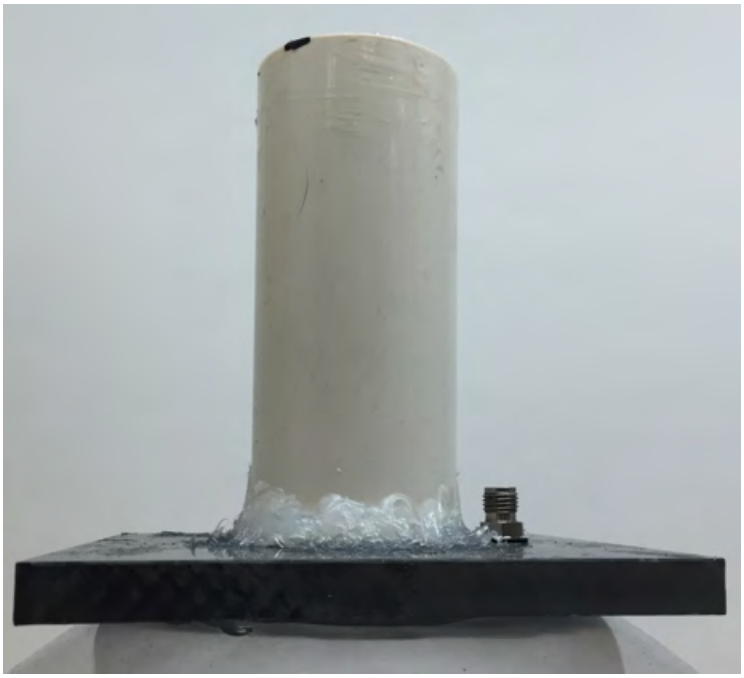


Figure 2.3: PVC neck and sheet, both glued to top of polycarbonate sphere.

2.3 Plumbing System

The plumbing system is made up of the vacuum line, air inlet line, refrigerant line, and pressure gauge line. The same plumbing system that was developed by Lomax is used with this polycarbonate testing vessel [3]. This system has all four lines joined together through a connection of a 3-port valve and a 4-port fitting. A pressure transducer was added for pressure measurements during tests by Klieger [6]. A picture of the plumbing tree is shown in Figure 2.4.

Contrary to the original configuration of ASTM E681 with the glass flask, the plumbing tree does not penetrate the rubber stopper, rather it penetrates through the threaded hole in the PVC sheet. A 1/4-inch NPT connection is wrapped in Teflon tape and threaded into the PVC sheet to ensure that it remains air-tight. This

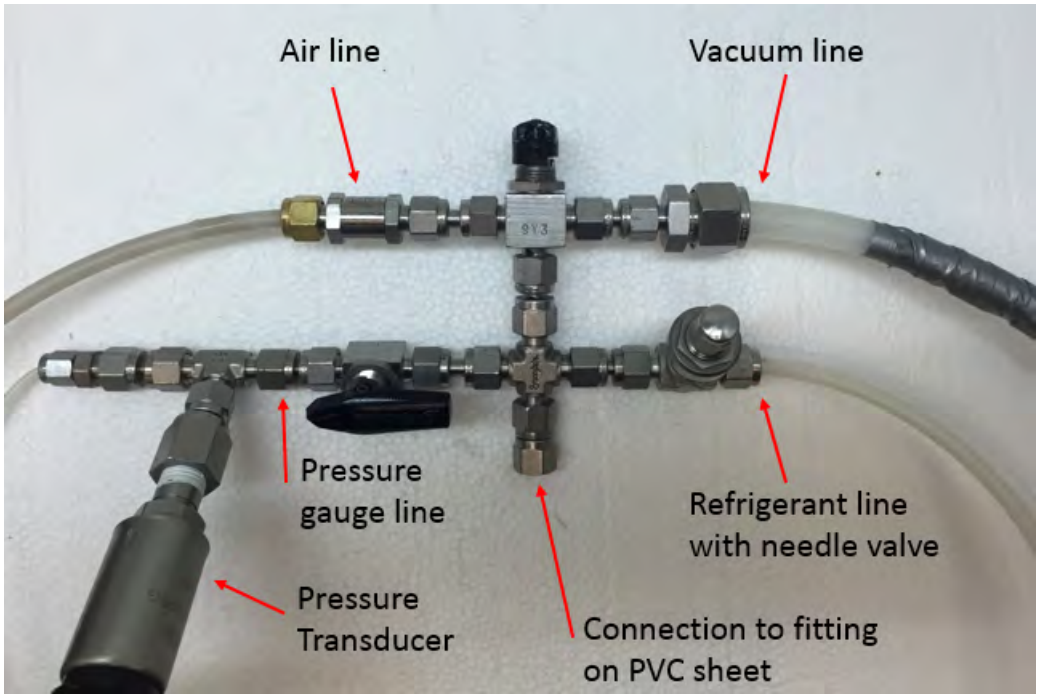


Figure 2.4: Plumbing tree, originally design by Lomax [3].

configuration carries many advantages over the previous design where the plumbing tree penetrated the rubber stopper. The penetration through the rubber stopper was vulnerable to leakage. The seal was secured with glue, but because the valves in the plumbing tree were often being adjusted, the seal was prone to leak. Also, the glue sealing the penetration was prone to breaking during the violent ejections of the rubber stopper during venting. This created issues when trying to achieve a vacuum in the flask and also allowed refrigerant to leak before testing, making it more difficult to ensure an accurate concentration of refrigerant is combusted. The threaded connection into the PVC sheet was a more efficient method for attaching the plumbing system and was used in the development of the polycarbonate testing apparatus.

2.4 Electrodes and Ignition System

The ignition system in the new polycarbonate apparatus uses the same system that was designed and built by Lomax [3]. This ignition system was designed with guidance from ASTM E681 and ASHRAE 34, but incorporated some deviations to improve its efficiency. One notable characteristic is the 0.2 s spark created between two tungsten wires. ASTM E681 specifies a 0.4 s spark gap ignition source but ASHRAE 34 [5] allows it to be shortened to 0.2 s if the flame propagation is still visible while the spark is active. Per ASTM E681 [1], the ignition system was powered with 30 mA at 15 kV.

Additional deviations to the electrodes were made in this apparatus in order to create additional testing benefits. Most notably, the electrodes no longer penetrate through the rubber stopper but instead penetrate through the side of the polycarbonate flask. A major advantage of the polycarbonate flask over glass is the ability to easily drill holes through it. The electrode rods that were used are 3.175 mm (0.125 in.) threaded stainless-steel. Two holes that were slightly larger than the threaded rods were drilled into the side of the polycarbonate flask at a distance to place the tungsten wires 1/3 of the diameter from the bottom of the flask, as specified by ASTM E681 [1]. The ends of the electrode rods that are on the outside of the flask were bent upwards to allow for a stable connection to the power supply. After the tungsten wires were firmly connected at the end of the electrode rods, the penetrations through the polycarbonate were sealed on both the inside and outside with silicone sealant. The glass coverings specified by ASTM E681 [1], which were

designed to avoid early arcing, were not included because no arcing between the electrode rods was observed. A picture of the new electrode configuration in the polycarbonate flask is shown in Figure 2.5.

Figure 2.5: New electrode configuration through the side of the polycarbonate sphere.

There are several advantages to having the electrodes enter through the side of the flask and not through the rubber stopper, as originally required by ASTM E681. One major advantage is that the electrodes are now removed from the flame path. This is beneficial to the flammability test in general, but most importantly for R-32 and other 2L refrigerants due to their long quenching distance. The quenching distance for R-32 is approximately 6.5 mm [7], which is much longer than other common fuels such as propane (1.70 mm) [7]. The electrode rods are spaced much

farther apart than 6.5 mm, but the large quenching distance supports the idea that the flames from refrigerant gases would be significantly affected by disruptions and heat sinks such as the electrode rods. This testing method relies on visual observation of the flame which will be negatively influenced if the flame is unable to propagate fully and evenly due to interference from the electrode rods.

Another advantage of this electrode configuration is the removal of the electrodes from the rubber stopper. The previous design for the electrodes created two additional leakage paths through the rubber stopper, as well as an unevenly distributed mass on the stopper. As previously described in Section 2.3, penetrations through the rubber stopper were prone to leaks due the significant disruption during venting. The seal on the new electrode configuration is not disturbed during venting and is designed to produce a more secure air-tight seal in the polycarbonate flask. Removing the electrodes (and plumbing system) from the stopper leaves zero additional mass and allows for an evenly distributed weight to be added, discussed in Section 2.5.

2.5 Weighted Rubber Stopper

As shown in previous work done by McCoy [4], a major concern with this testing standard was the possibility for the rubber stopper to vent the flask before the flame was able to fully propagate, causing a significant disruption in the flame propagation. Also, when conducting tests at atmospheric pressure, the old rubber stopper was prone to leak and disrupt the mixture composition before ignition [4]. In an attempt

to ensure venting did not occur until the flame propagated to the flask's walls, as well as minimize leakage from occurring at atmospheric pressure, an additional mass was added to the rubber stopper. The new polycarbonate apparatus allows the rubber stopper to sit on top of the PVC neck with no penetrations or fittings. This allowed for an easy application of mass that was evenly distributed across the surface of the rubber stopper. The final component of the stopper was a thin layer of vacuum grease that was applied periodically. The grease helped to maintain a seal, especially near atmospheric pressure.

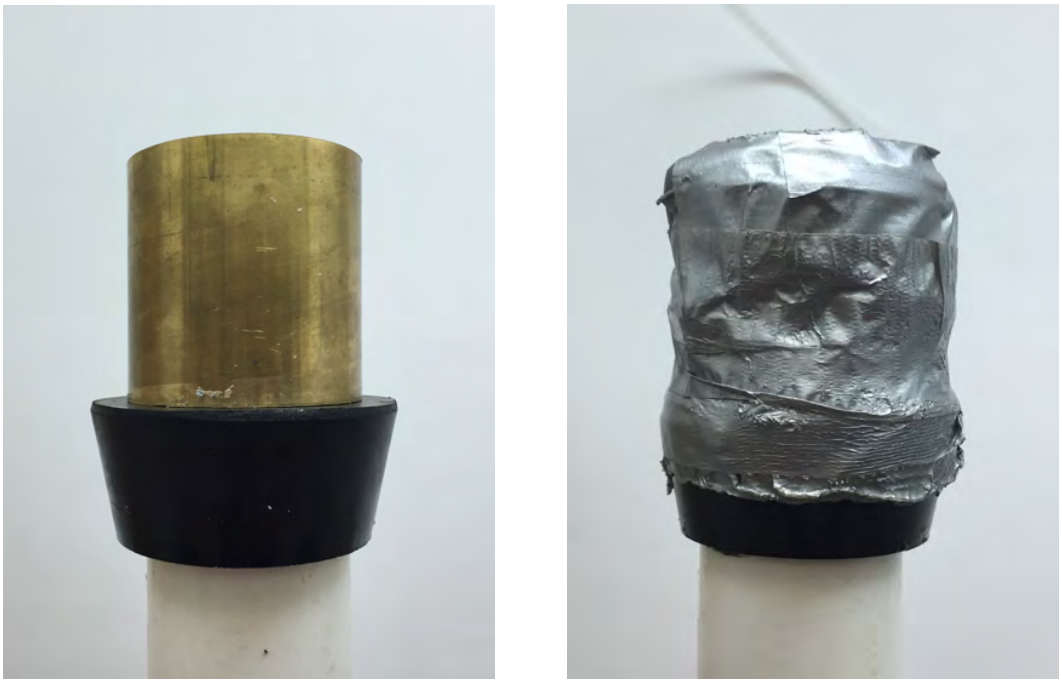
In collaboration with work done by Alexandra Klieger [6], a specified mass was calculated to yield a consistent venting pressure from the flask. It was envisioned that the additional weight would allow the flammability tests to start and end at an average of atmospheric pressure conditions, e.g. starting at 91.2 kPa (0.9 atm) and ending at 111.5 kPa (1.1 atm). The interior diameter of the PVC neck was 5.25 cm, and the area from this opening was used to calculate the additional mass needed for an extra 0.1 atm (10.1325 kPa) of pressure using:

$$F = AP \tag{2.1}$$

Where F is the force needed (N), A is the surface area of the neck opening (m^2) and P is the desired extra pressure (Pa). Applying the parameters of the neck opening and desired pressure yields a force (F) of 21.94 N. Using an assumed acceleration due to gravity of 9.81 m/s^2 yields:

$$M = \frac{21.94N}{9.81m/s^2} = 2.24kg \tag{2.2}$$

The additional weight that was added to the rubber stopper was a solid cylindrical piece of brass with a diameter of 7.0 cm. The brass was wrapped in rope and stacked on top of the rubber stopper. The rope was included in the stopper assembly as a means to secure the stopper after venting and prevent it from damaging the apparatus. This will be further explained in Section 2.6. The entire assembly of the mass, rope, and rubber stopper was secured with duct tape. A picture of the stopper assembly with and without duct tape is shown in Figure 2.6.



(a) No rope and no duct tape (b) With rope and duct tape

Figure 2.6: Size 14 rubber stopper with brass weight on top.

The piece of brass used as the additional mass was already present in the laboratory and unable to be adjusted exactly to the desired mass. The total assembly of

the weighted stopper was 2.48 kg, slightly larger than the 2.24 kg calculated above. The venting pressure calculated from a 2.48 kg stopper is 11.25 kPa (0.11 atm). The venting pressure from the weight of the stopper assembly was determined to be sufficiently close to the originally desired venting pressure. After analyzing initial tests with the weighted rubber stopper, Klieger showed that the flask vented inconsistently, but did so at significantly higher pressures than 111.5 kPa for mixtures near the lower flammability limit [6]. The weighted rubber stopper did not create the consistent venting pressure that was desired, but it did aid in ensuring that the flask vented well after the flame propagated to the walls of the flask. The weighted rubber stopper was used for the remainder of the flammability limit tests.

2.6 Platform and Stirring System

The same stirring system that was developed by Lomax [3] was used in this polycarbonate apparatus. The stirring bar, magnet, and propeller blade were removed from the glass flask and inserted into the bottom of the polycarbonate flask.

There was a significant change in mounting the polycarbonate flask compared to how the previous glass flask was mounted. Previously, the glass flask was mounted by a clamp around its neck and secured in a stainless-steel and aluminum framed box, designed per ASTM E681. The neck of the glass was not a separate part from the body, and also had a slightly thicker lip at the top, making clamping the flask from the neck a viable and secure option. A picture of the glass flask mounted inside of the testing box is shown in Figure 2.7.

Figure 2.7: Glass flask mounted with clamp around neck in apparatus enclosure. Stopper and electrodes are not present here.

As explained in Section 2.2, the neck of the flask was a piece of PVC pipe that was glued to the polycarbonate sphere, and the PVC pipe had no thick lip at its end that would safely secure the clamp used on the glass flask. Due to the differences in neck shape and construction, it was determined that the polycarbonate prototype should be supported from the bottom of the sphere. This created an issue because the bottom of the sphere must sit with adequate space underneath it for the magnetic stirrer to control the stirring system inside the flask. To secure the flask from the bottom while also leaving space for the magnetic stirrer, an elevated piece of plywood was used to mount the polycarbonate flask. A hole approximately

13 cm in diameter was cut into the plywood to leave space for the stirrer. The polycarbonate flask was glued to a PVC ring, roughly 2.5 cm tall, 6 mm wide, and 15 cm in diameter. Then, the PVC ring was glued to the plywood around the 13 cm hole. The plywood was elevated with 4 pieces of 5x10 cm wood that were secured with screws. This allowed for the magnetic stirrer to rest under the plywood and adequately operate the stirring system.

The final piece of the platform that needed to be developed was the pulley system for the weighted rubber stopper. The goal for the pulley system was to keep the weighted stopper from damaging any components of the apparatus after it vents and is ejected off of the PVC neck. The pulley system was made from a piece of 5x10 cm wood that raised approximately 0.6 m from the plywood platform. The bottom of this was screwed to a perpendicular piece of wood that was then clamped to the plywood platform. At the top of the 0.6 m piece of wood was a plastic ring that was attached with duct tape. The rope that was connected to the stopper ran up through the plastic ring then came down and out through the bottom of the hood window. The rope is secured by an operator standing outside of the hood during a test to keep the stopper from falling after venting. A picture of the polycarbonate apparatus mounted on the wooden platform with pulley attached is shown in Figure 2.8.

This platform and pulley system were designed as a temporary system to allow for testing at room temperature in the polycarbonate flask. This is not the intended long term solution for the polycarbonate flask. In future work, the polycarbonate flask, support system, and pulley system will be adjusted so that the polycarbonate

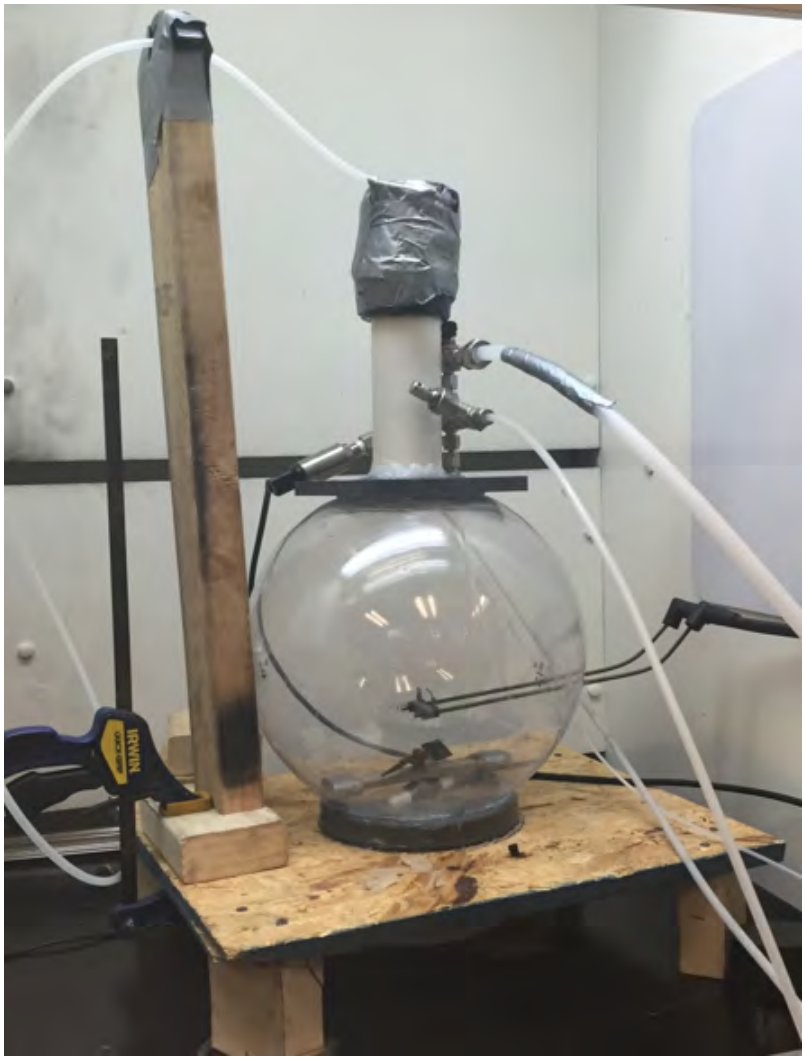


Figure 2.8: Full polycarbonate apparatus mounted on wooden platform with pulley attached.

flask can sit in the same insulating chamber that was designed for the 12 L glass flask. Being in the insulated chamber would allow for testing at elevated temperatures and would also offer an added layer of protection. A proposed design of a new enclosed mounting system without wood is shown in Chapter 4.

2.7 Test Conditions and Procedure

Previous work has shown that flammable refrigerants can be sensitive to testing conditions including humidity and temperature. Several refrigerants have different flammability limits based on the humidity of the air. It has been shown that R-32 is unaffected by humidity [23]. However, dry air was used in each test with R-32 to maintain consistency. The air was dried using a desiccator that was implemented by Lomax [3]. Tests were conducted at atmospheric pressure (101.3 kPa), as specified by ASTM E681 [1], as well as 91.2 kPa. Testing was done at 91.2 kPa to determine how the lower starrting pressure would affect the LFL. Also, all tests were conducted at room temperature. The polycarbonate apparatus has no enclosure that can maintain a specified temperature, making testing at exactly 60 °C not feasible. These tests are meant to represent testing at 23 °C as specified by the standard [5], although the exact temperature in the lab on each day of testing varied. It was assumed that the slight variation in room temperature would have no significant effect on the test results.

A detailed standard operating procedure (SOP) for testing with the original ASTM E681 apparatus at the University of Maryland was prepared by Lomax [3]. The majority of the SOP remains unchanged because the polycarbonate apparatus utilizes the same stirring system, ignition system, and plumbing system that was developed by Lomax. The main difference is that the polycarbonate apparatus requires an operator to hold the rope connected to the weighted rubber stopper and ensure the stopper does not fall and damage any components. In future work, the

weighted stopper will be secured automatically and there will be no need for an operator to directly interact with the apparatus during testing. A proposed design to automatically secure the weighted rubber stopper with a magnet is shown in Chapter 4.

To capture the video, a high speed camera was used. The camera used was an Exilim EX-FH100 high speed camera manufactured by Casio. The camera was set to record at 120 frames per second for each test.

Chapter 3: Results

3.1 Vacuum Leak Test

After construction of the polycarbonate prototype, the next step was to determine if it could reach and hold a vacuum according to the requirements of the test standard. ASTM E681 requires that the vessel be evacuated to a gauge pressure of -100 kPa before introduction of fuel and air. The maximum allowable leak rate for the vessel is 0.1 kPa/min while isolated under a vacuum [1]. In order to ensure that the air-tight integrity of the polycarbonate vessel did not degrade over time, a leak test was performed immediately after construction, as well as prior to the conclusion of all the tests from this research project. The results from the two leak tests are shown in Figure 3.1. The pressure inside of the vessel was normalized to account for daily variations in barometric pressure. In each test, the vessel was pulled to a vacuum and then the vacuum pump valve was closed. The vessel settled for 5 minutes and then the pressure was recorded in 5 minute increments for 15 minutes.

The starting pressures and average leak rates are summarized in Table 3.1. Both tests showed that the polycarbonate apparatus exceeded the vacuum requirements of ASTM E681. Also, it shows that no significant damage occurred to the seals of the apparatus over time. 68 tests were conducted in the time frame of this

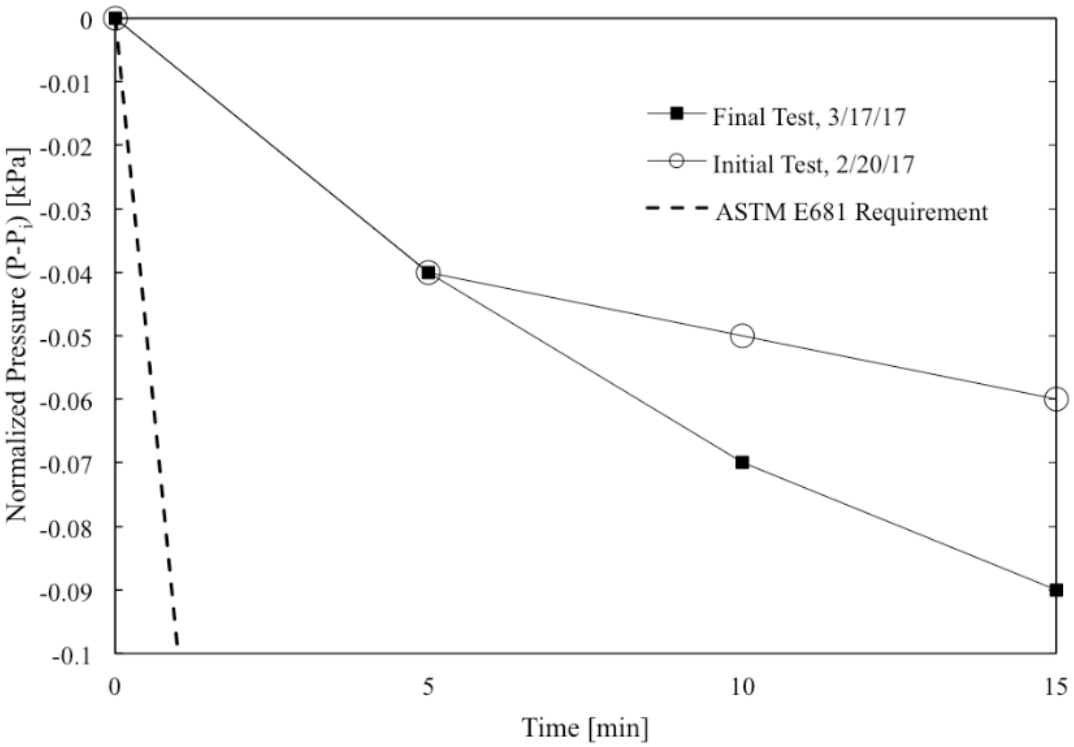


Figure 3.1: Normalized vacuum pressure in polycarbonate vessel vs. time.

research, and the average leak rate only grew 0.002 kPa/min. These tests prove that the polycarbonate flask can hold an adequate vacuum, and therefore can be filled with an accurate mixture of fuel and air via partial pressure measurements.

Table 3.1: Summary of vacuum performance.

Test	**Max. Vacuum Pressure [kPa]**	**Avg. Leak Rate [kPa/min]**
Initial Test, 2/20/17	-100.65	0.004
Final Test, 3/17/17	-101.80	0.006

3.2 Effects of Weighted Stopper

The weighted stopper proved to be an effective way to improve venting in the polycarbonate apparatus. The video analysis of tests along with pressure data acquisi-

tion [6] showed that the flask consistently vented well after the flame reached the wall (albeit not at a consistent pressure). Using the difference in frames from the video (shot at 120 frames per second), the time difference between the flame hitting the wall and venting was measured for each test. The results of the various time differences are shown in Figure 3.2.

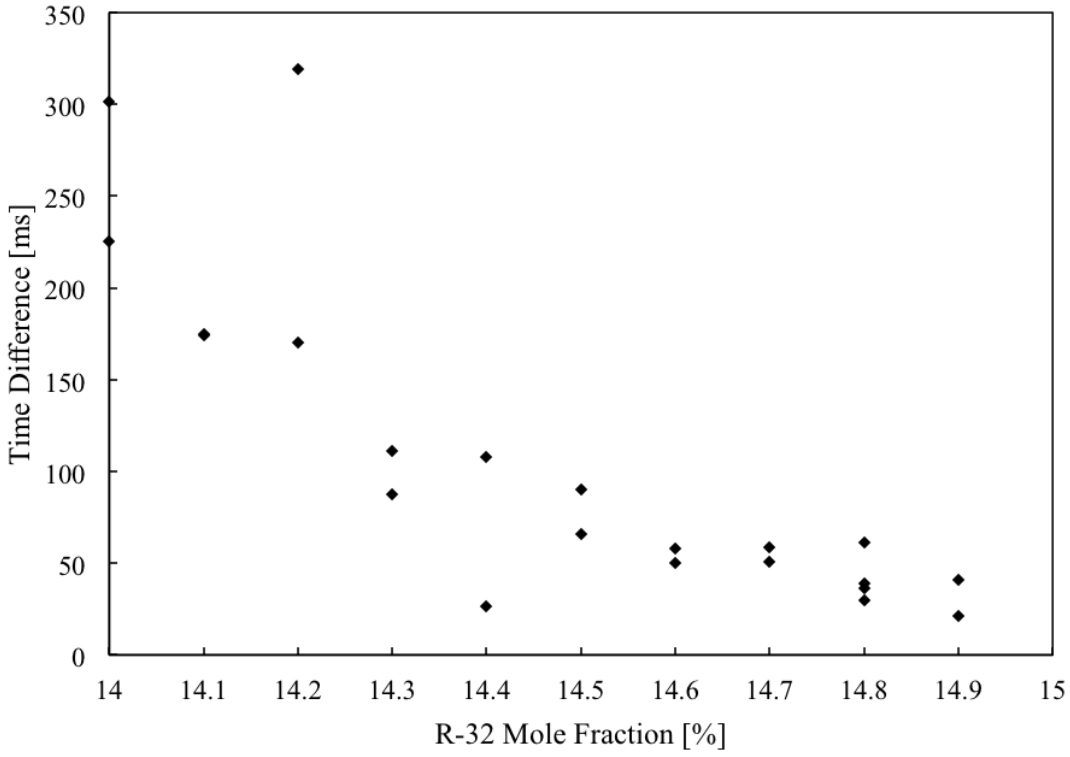


Figure 3.2: Time difference between when flame hits the wall and when venting occurs vs. mole fraction of R-32, from tests at atmospheric starting pressure.

Figure 3.2 shows that all of the time differences are positive. In every test the polycarbonate flask vented after the flame reached the wall. The time difference generally decreases with concentration, and it is anticipated that venting might begin to occur before the flame hits the wall as the concentration moves closer to a stoichiometric condition. This trend is related to the increase in temperature and

moles of R-32, and is further explained by Klieger [6]. For the case of determining the LFL of R-32, the weighted stopper proves to consistently ensure that venting occurs after the flame reaches the wall. However, the short time difference at high concentrations contributed to the motivation for testing at a starting pressure of 91.2 kPa. Starting the test at a lower pressure would provide additional time for the flame to propagate to the wall before venting occurs. This is further supported in work by Klieger [6].

Another purpose of the weighted rubber stopper was to ensure that tests could be conducted at atmospheric pressure without significant leakage. This has been an ongoing issue among laboratories and has even forced some to conduct tests at -2 kPa to ensure no significant leaking is occurring before ignition [4]. To ensure that tests at atmospheric pressure were possible, a leak rate test was conducted at 1 kPa (gauge), with pressure recorded in 5 minute increments for 15 total minutes. Before the test began, a full vacuum was reached inside of the flask and then dry air was introduced until the pressure was 1 kPa. The flask was settled for several minutes and then the test began. The results of the leak test are shown in Figure 3.3. The average leak rate from this leak test was 0.017 kPa/min. While this leak rate is larger than the leak rates determined at full vacuum, it is still well under the 0.1 kPa/min requirement [1] and indicates accurate testing can be conducted at atmospheric pressure, even with long mixing and settling times.

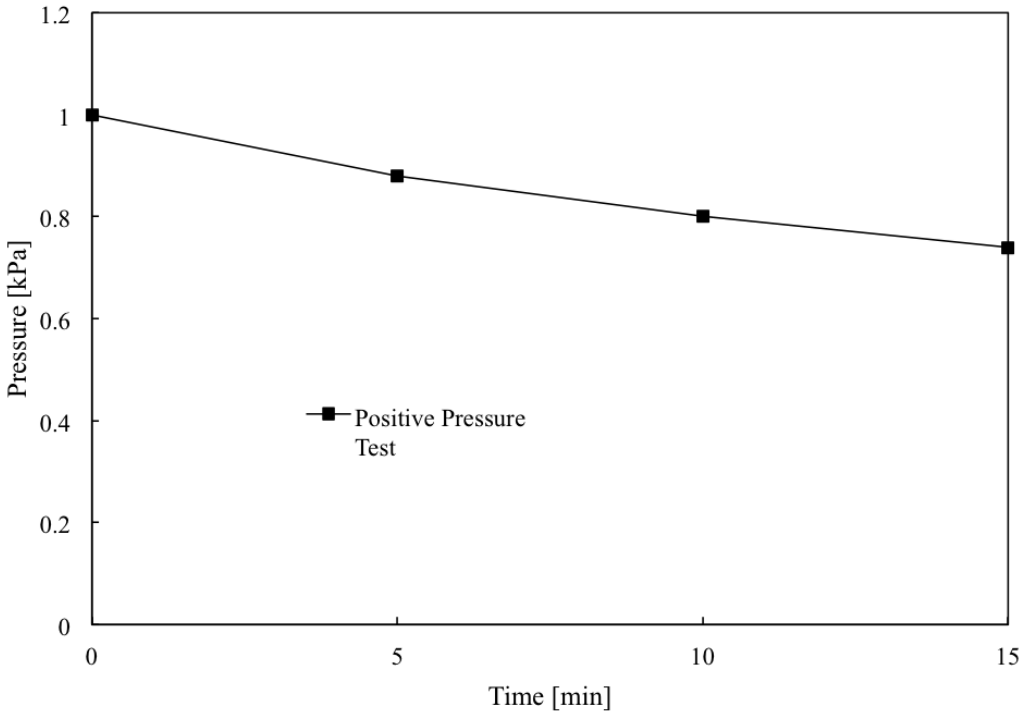


Figure 3.3: Positive pressure in polycarbonate vessel vs. time.

3.3 Reproducing Lower Flammability Limit

To prove that the polycarbonate apparatus is a suitable replacement to the glass flask, an accurate lower flammability limit must be able to be produced. The lower flammability limit of R-32 was reproduced using the direct flame angle measurement approach that was proposed by McCoy [4]. In summary of this approach, the first frame when the spark is visible and the frame when the flame hits the wall are paired next to each other aligned and at the same magnification in Microsoft PowerPoint. Then, a line is drawn from the spark frame to the frame where the flame hits the wall to identify the origin of the flame. The PowerPoint file was converted to .PNG format to allow for ImageJ software to analyze it. ImageJ software is used to draw

an angle of the flame with the apex at the ignition point. The angle is measured 10 times and the average value is taken to be the flame angle for that flame [4]. A sample image of the flame angle measurement for a flammable mixture is shown in Figure 3.4. A sample image for the measurement of a non-flammable mixture is shown in Figure 3.5.

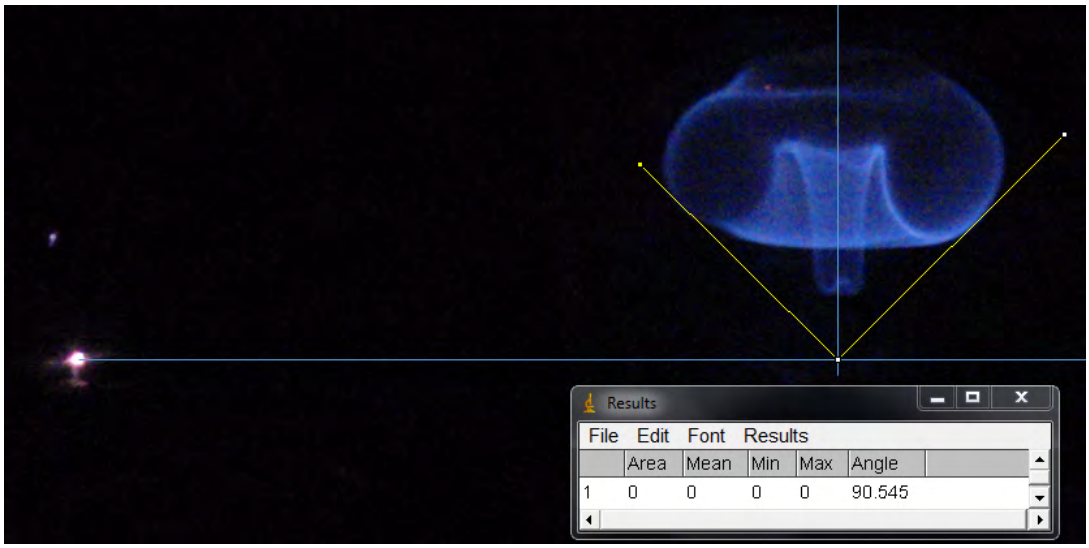


Figure 3.4: Sample flame angle measurement of 14.6% R-32, 101.3 kPa starting pressure.

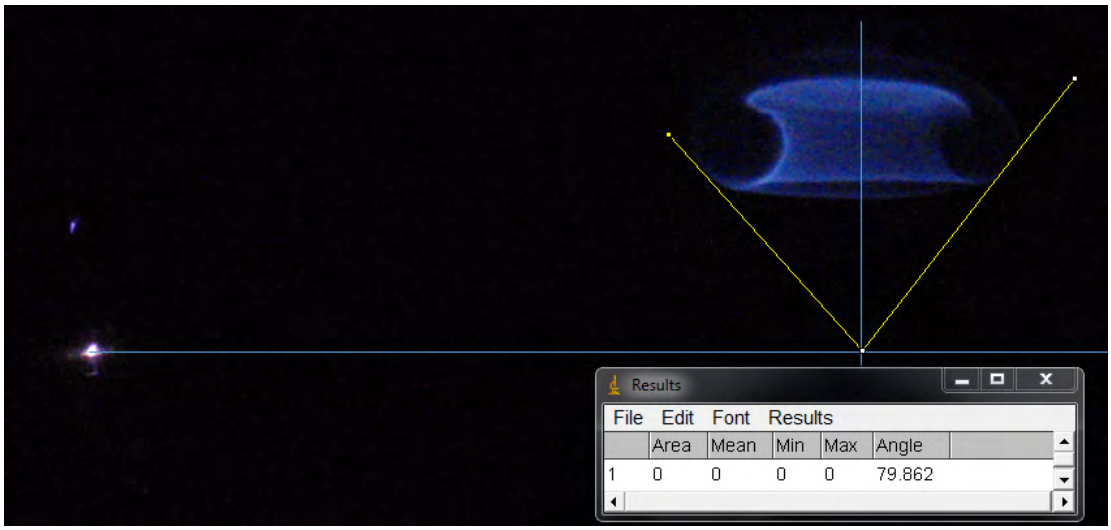


Figure 3.5: Sample flame angle measurement of 14.4% R-32, 101.3 kPa starting pressure.

The direct flame angle measurement allows for the flame angle to be plotted against mole fraction of fuel. A linear best fit line is applied to the data points to obtain the mole fraction when the best fit line intersects with 90°. This intersection in considered the LFL of the fuel [4]. The main benefit of this analysis is that several flame angle measurements get incorporated into the determination of the LFL, opposed to only those that surpass 90°, as specified by the test standard [1, 5].

An additional benefit of utilizing this analysis method is that it allows for a calculation of a confidence interval with the flammability limit results. From McCoy's work in the glass flask, a lower flammability limit of 14.74 ± 0.12% was calculated with 95% confidence [4]. The plot of flame angle vs. mole fraction of R-32 from McCoy's thesis is reproduced in Appendix A. The ± 0.12% with 95% confidence serves as a benchmark for the new polycarbonate vessel to see if it can reproduce an LFL with a range less than or equal to 0.12% at 95% confidence.

Multiple tests with R-32 were conducted at an atmospheric starting pressure between 14.0% and 14.9% concentration, increasing in increments of 0.1%. The flame angles from these tests are shown in Figure 3.6. A linear best fit line was used to find the intersection at 90°. The 95% confidence interval curves are also shown. The analysis of the flame angles from the tests in the polycarbonate vessel yield an LFL of 14.6% (14.57 ± 0.07%). This value is 0.17% lower than the LFL reported by McCoy, and also has a lower variance range at 95% confidence.

It should be noted that if the traditional method for determining flammability was used, as defined by the test standard, the LFL would also have been 14.6%. Two of three tests at 14.6% measured at least 85°. The standard states that the

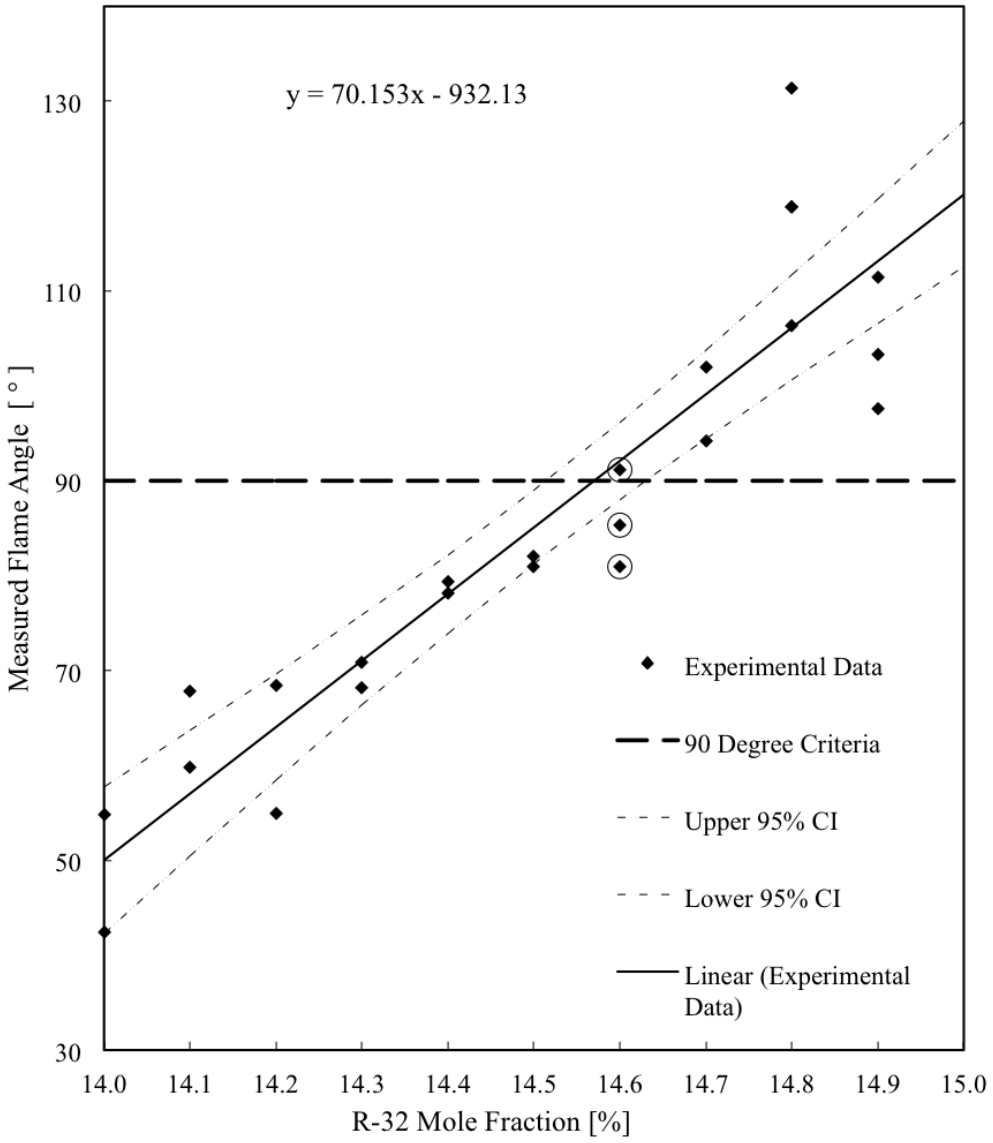


Figure 3.6: Measured flame angle vs. mole fraction of R-32, from tests at 101.3 kPa.

critical flame angle for flammability is 90°± 5° [5]. The three tests at 14.6% are highlighted in Figure 3.6 with a circle around the marker. This 10° variability is not present in the direct flame angle measurement technique described above. The flammability limits that were produced by the polycarbonate vessel are comparable to previous results by McCoy as well as values published in literature [4]. In terms

of recreating the correct LFL for R-32, the polycarbonate apparatus proved to be a capable alternative.

In Klieger's thesis [6], the affect of starting pressure on the flammability limit and venting was investigated. To support this work, flame angle measurements were taken at various concentrations for starting pressures of 81.1 kPa and 91.2 kPa. Klieger showed minimal difference in pressure rise measurements between tests at 91.2 kPa and 101.3 kPa. Flame angle measurements from tests at 91.2 kPa were comparable to results from atmospheric tests. The flame angles from the 91.2 kPa tests are plotted against the mole fraction of R-32 in Figure 3.7. This plot yields an LFL of 14.8% (14.84 $\pm$ 0.09%). This LFL is within 0.2% of the LFL determined from testing at atmospheric pressure. ASTM E681 specifies that the LFL must be repeatable with a 0.2% variation within the same lab [1]. The starting pressures of 101.3 kPa and 91.2 kPa yielded comparable LFL results with a minimal difference, showing that the pressure results measured by Klieger are supported by the flame angle measurements. Testing with a starting pressure slightly below atmospheric provides several advantages for consistency between laboratories, especially for locations where the atmospheric pressure may be well below 101.3 kPa. The starting pressure of 91.2 kPa is recommended for incorporation to the standard.

The analysis of results from 81.2 kPa tests were not a direct component of this thesis, but the additional tests contributed to the durability analysis of the polycarbonate apparatus. This explains why not all 68 tests are included in the LFL calculation for R-32. The flame angle results for tests at an 81.2 kPa starting pressure are shown in Appendix A.

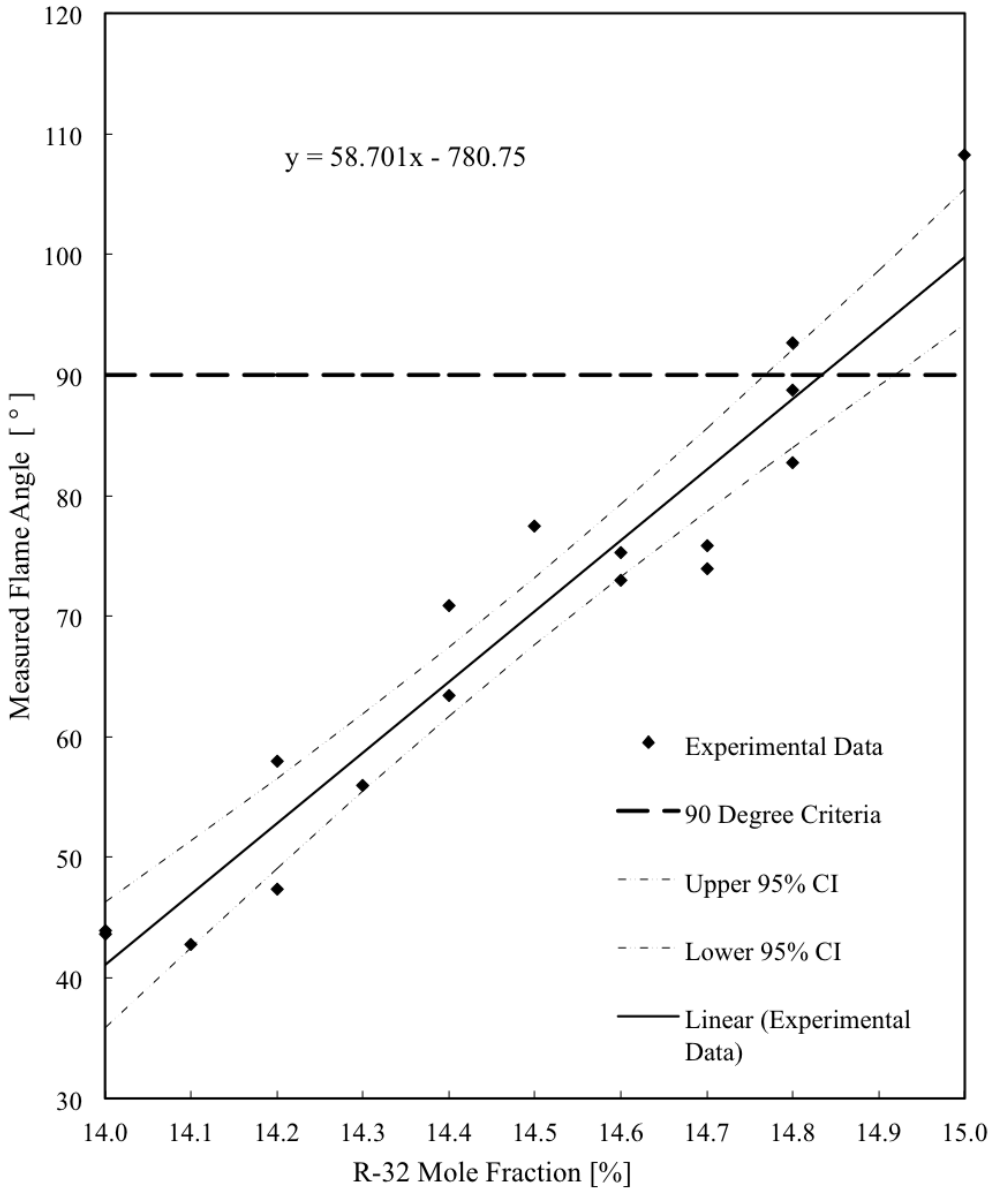


Figure 3.7: Measured flame angle vs. mole fraction of R-32, from tests at 91.2 kPa.

3.4 Effects of Electrode Placement on Flame Angle

A major advantage of the polycarbonate vessel is that it enabled the electrode rods to be drilled through the side of the flask and removed from the flame path. This

allowed for the quenching effects of the electrode rods to be quantified based on flame angle measurements. Klieger [6] conducted further analysis of the electrode rods quenching effects based on the changes in pressure rise in the flask. During the initial testing in the polycarbonate flask, the measured flame angles were consistently larger than the previously reported angles from tests in the glass flask [4]. This is summarized by the comparison of the linear best fit lines that were produced by flame angle measurements in the glass [4] and polycarbonate. The two linear fit lines are shown in Figure 3.8. Also in this plot is the difference in the flame angle measurements, which shows a linear increase with concentration of R-32.

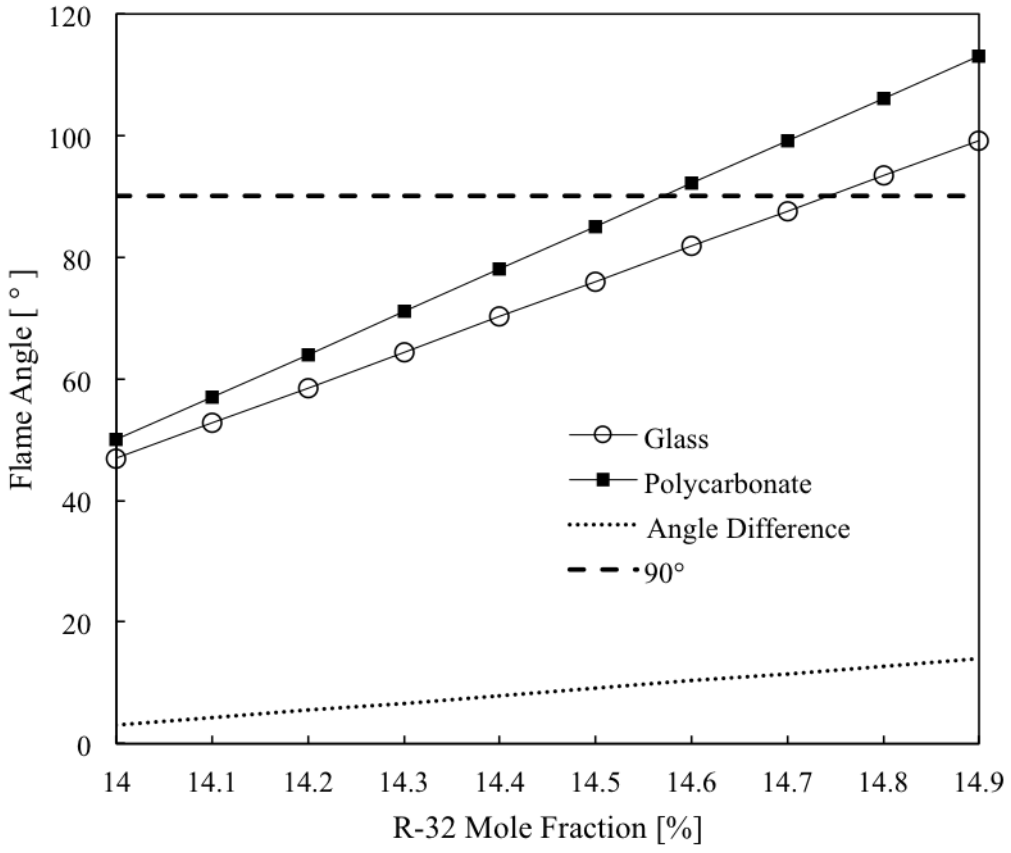


Figure 3.8: Linear best fit of flame angle measurements vs. mole fraction of R-32, all data from tests at 101.3 kPa starting pressure.

To better understand this, two additional stainless steel threaded rods, the same size as those used for the electrode rods, were attached to the weighted stopper in the polycarbonate flask. These rods effectively simulated the quenching effect of the electrodes that was occurring in the ASTM E681 glass flask apparatus. A picture of the rubber stopper with the extra electrode rods is shown in Figure 3.9. The polycarbonate apparatus with the extra electrodes is shown in Figure 3.10.

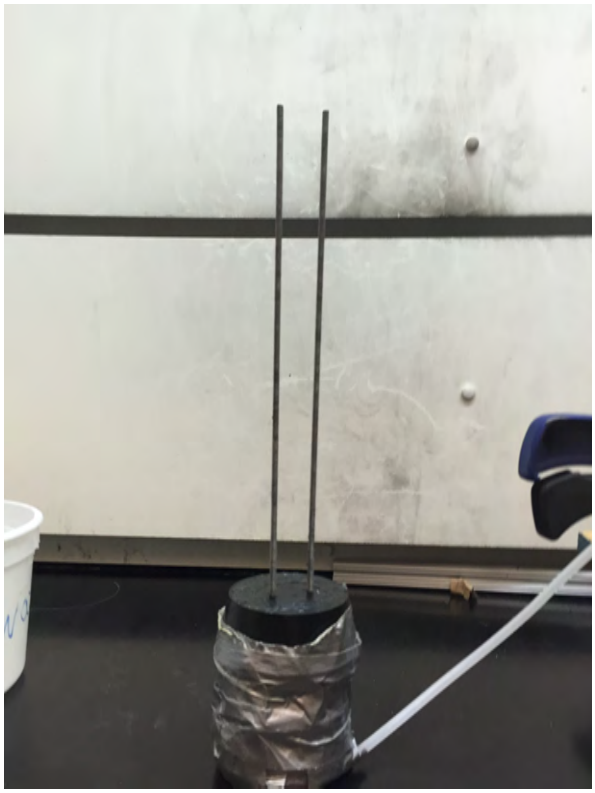


Figure 3.9: Weighted rubber stopper with extra electrode rods.

Flame angles from tests in the glass flask were initially used for comparison, but the previous glass flask had several differences that could have attributed to changes in flame angles. With the extra rods in the new polycarbonate flask, the only variable that changed between the testing was the additional electrode rods. The extra electrode rods were included in several tests with R-32 concentrations

Figure 3.10: Polycarbonate apparatus setup with extra electrode rods.

of 14.0, 14.4, and 14.8% at an atmospheric starting pressure. The resulting flame angles, as well as the flame angles from tests without the extra electrode rods, are shown in Figure 3.11. In this figure, the tests with extra vertical electrode rods are labeled as "quenched", and tests without the extra rods are labeled as "non-quenched".

As shown in the Figure 3.11, the effects of quenching from the electrodes increases as the concentration of R-32 increases. The average difference between

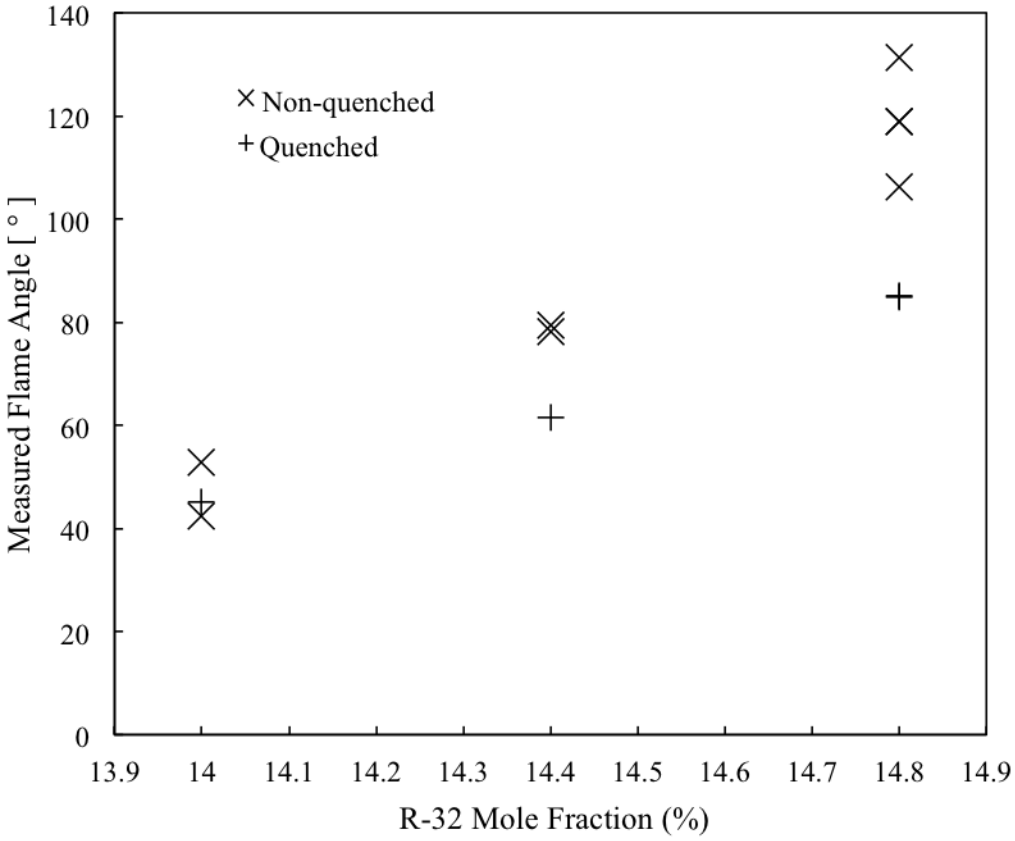


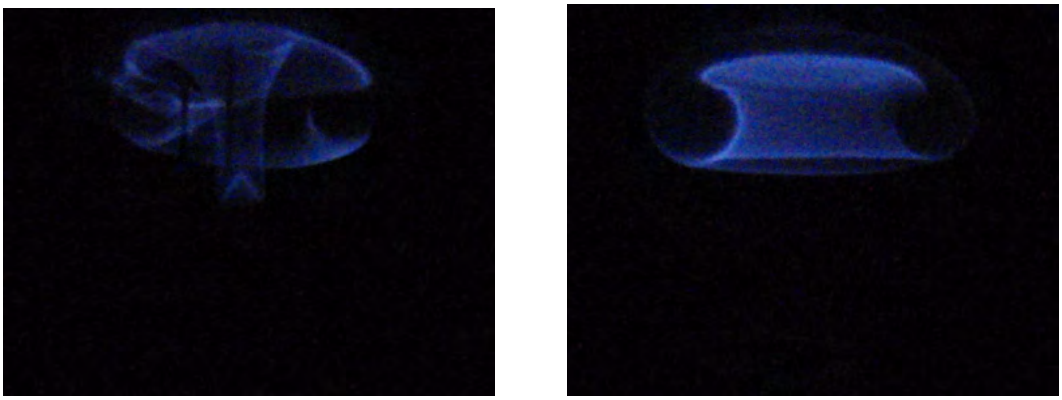
Figure 3.11: Quenched (from prototype with additional vertical rods) and non-quenched (from prototype) average flame angle vs. mole fraction of R-32, 101.3 kPa starting pressure.

quenched and non-quenched flame angles is shown in Table 3.2. Side-by-side images of these flames provides a good visual representation of the effects from the electrodes. In addition to limiting the measured flame angle, the brightness and shape of the flames are affected by the electrode rods, especially at higher concentrations. Figure 3.12 shows the quenched and non-quenched flame of an R-32 concentration of 14.4%. This shows an increased effect from the impinging electrode rods. Figure 3.13 shows the quenched and non-quenched flame of an R-32 concentration of 14.8%. This shows the drastic difference that the electrode rods have on the size and

shape of the flame when it reaches the vessel walls. The quenched and non-quenched flames of an R-32 concentration of 14.0% were both very dim and differed very little in size and shape, rendering a side by side comparison useless. This comparison shows little effect from the electrode rods.

Table 3.2: Average flame angle difference of quenched and non-quenched flames.

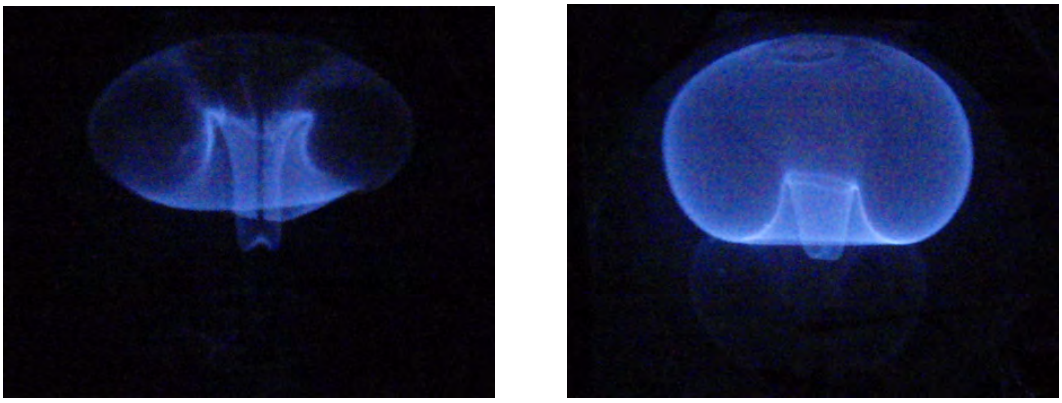
R-32 Concentration	**Average Difference in Flame Angle [°]**
14.0%	2.6
14.4%	17.3
14.8%	33.8



(a) Quenched (b) Non-quenched

Figure 3.12: Quenched and non-quenched flames from 14.4% concentration of R-32, 101.3 kPa starting pressure.

The quenching effect from the electrode rods has a significant impact on the measured flame angles. This difference yields a smaller LFL for R-32. Previous work by McCoy reported an LFL of 14.74% [4], which corresponds closely to the "quenched" flame angle of 14.8% shown in Figure 3.11. However, the LFL determined from non-quenched flames in the polycarbonate vessel at an atmospheric starting pressure was 14.6%. The removal of the electrode rods from the flame path



(a) Quenched (b) Non-quenched

Figure 3.13: Quenched and non-quenched flames from 14.8% concentration of R-32, 101.3 kPa starting pressure.

yields a lower LFL for R-32, as well as provides brighter and more symmetrical flames allowing for easier flame angle analysis. The vertical electrodes weaken the flames and result in a higher, and less accurate, measure of LFL.

One key note about the LFL determined in this work is that the spark gap duration was lowered from 0.4 s to 0.2 s. This was because McCoy and Lomax observed the spark gap over driving the flame propagation in the flask when the gap was at 0.4 s [3, 4]. The lowered spark gap duration caused a slightly higher LFL for R-32 than the reported value by ASHRAE of 14.4% [24]. This is supported by work by Kul [8], who found an LFL of 14.7% when using a spark gap with reduced power. In summary, the LFL's from McCoy, Kul, and ASHRAE are compared to the LFL from this work in Table 3.3. It should be noted that the value from this work in the table is from tests at atmospheric starting pressure. Testing at 91.2 kPa yielded a slightly higher LFL of 14.8%, but this was not included to maintain consistency in this comparison (all other values are from tests at atmospheric starting pressure).

Also, there are several other values for R-32's LFL that are lower than ASHRAE's 14.4%, but only the higher values were used for this comparison.

Table 3.3: Reported LFL values for R-32.

R-32 LFL [%]	**Reference**	**Notes**
14.4%	ASHRAE [24]	Reported value from ASHRAE, 0.4 s spark gap
14.6%	This work	No quenching from electrodes, reduced spark duration
14.7%	Kul [8]	Reduced spark power
14.7%	McCoy [4]	Burst disc, reduced spark duration
14.8%	McCoy [4]	Rubber stopper, reduced spark duration

Based on the values in Table 3.3, the LFL from this work is lower than other reported values that utilized some form of a weaker spark gap (shorter duration or reduced power). Direct comparison cannot be made to the value reported by ASHRAE because of the difference in the ignition spark gap. However, it is clear that the quenching has skewed the reported LFL values of R-32, and likely has impacted the values for other 2L refrigerants as well.

Other refrigerants have quenching distances that are even higher. One notable example is R-1234yf, which has a reported quenching distance as high as 24.8 mm [7]. This is almost 4-times as high as the reported value for R-32. The reported LFL values for R-1234yf may be extremely skewed because of the quenching by electrode rods, more so than the differences shown for R-32. The electrode rods quench the flame propagation when placed vertically in the testing apparatus, and it is important they are removed to allow for an accurate determination of a fuel's LFL.

3.5 Performance of Apparatus at Elevated Temperature

ASHRAE 34 states that single-compound refrigerants, as well as refrigerant blends, shall be initially tested at 60 °C. It is not until after flame propagation occurs at the elevated temperature that testing continues at 23 °C [5]. It has been found that the flammability limits of refrigerants widen with increased testing temperatures [23]. Other work in literature has even suggested refrigerant flammability tests to take place at as high as 100 °C in order to represent a worst case scenario [24]. All of the testing compiled in the polycarbonate apparatus occurred at room temperature (23 °C). It is important that the polycarbonate apparatus can be confidently used in testing conditions above 23 °C to meet the testing requirements of ASHRAE 34.

Based on the components of the polycarbonate apparatus, there is a possibility for degradation of the PVC as well as formation of leaks in the glue seals when exposed to long durations of elevated temperatures. In order to test this, the polycarbonate apparatus was placed inside an oven at 60 °C for 45 minutes. 45 minutes was chosen as a conservative estimate for exposure in an actual flammability limit test. A picture of the polycarbonate apparatus inside of the oven is shown in Figure 3.14. After the 45 minutes, the apparatus was removed from the oven. The rubber stopper was placed on top and a vacuum was reached. After the vacuum was reached, the leak rate was monitored to ensure that the integrity of the polycarbonate apparatus was not compromised. The leak rates before and after the oven exposure are shown in Table 3.4.

After the polycarbonate apparatus was exposed to 60 °C for 45 minutes, the

Figure 3.14: Polycarbonate apparatus in oven.

Table 3.4: Vacuum performance before and after 45 minute exposure to 60 °C.

Test	**Max. Vacuum Pressure [kPa]**	**Avg. Leak Rate [kPa/min]**
Before Oven Exposure	-101.80	0.006
After Oven Exposure	-102.20	0.003

leak rate at a full vacuum was relatively unchanged. This experiment simulated the elevated temperature exposure required by ASHRAE 34, and the entire polycarbonate apparatus maintained its integrity while no leak paths were formed. It should be noted that only one 45 minute exposure to 60 °C was performed. This test does not definitively prove that the apparatus will hold up to a series of tests at 60 °C. It is possible that after continual exposure to these conditions, some part of the apparatus could degrade and cause the apparatus to fail. This will need to be re-evaluated once the polycarbonate is setup in a testing enclosure that can be heated during testing.

It is recommended that test temperature higher than 60 °C not be conducted

in this current prototype because of its PVC neck. Based on the glass transition temperature of PVC (80 - 85 °C) and its thermal degradation temperature (83 °C), testing at higher temperature could jeopardize the integrity of the apparatus. It is recommended that a different material be used for the neck for future prototypes. A suitable replacement in this case would be to construct a similarly shaped neck out of polycarbonate, which does not degrade until temperatures well over 100 °C.

3.6 Durability of Polycarbonate Apparatus

The polycarbonate apparatus proved to be extremely reliable throughout all of the testing done. In total, 68 flammability limit tests were conducted in the apparatus. After all of the tests, there were no signs of etching or loss of transparency in the polycarbonate. The only change to the polycarbonate was a small amount of vacuum grease residue that splashed onto the walls of the sphere during testing. After this residue was noticed, the stopper was cleaned periodically to alleviate any significant build-up of vacuum grease and prevent any more splashing onto the walls. No surface reaction from HF was observed on either the polycarbonate or PVC components of the apparatus. This is a significant improvement from the glass flask, which showed signs of etching after 1-2 tests. Figure 3.15 shows a side by side comparison of a previously used glass flask before any tests and after 10 tests. Figure 3.16 shows the polycarbonate sphere before any tests and after 68 tests. The comparison shows a significant loss in transparency after 10 tests in the glass flask, while the polycarbonate sphere shows little to no loss in transparency after 68 tests.

(a) New glass flask

(b) Glass flask after 10 tests

Figure 3.15: Comparison of the glass flask before any tests and after 10 tests.

(a) New polycarbonate sphere

(b) Polycarbonate sphere after 68 tests

Figure 3.16: Comparison of the polycarbonate sphere before any tests and after 68 tests.

Another component of the polycarbonate apparatus that showed strong durability was the glue seal that was used to attach the PVC pipe to the the PVC sheet, the PVC sheet to the top of the polycarbonate sphere, and also seal the penetration

of the electrode rods through the side of the sphere. After 68 tests and a 45 minute exposure to 60 °C, the apparatus was still able to hold a seal at full vacuum.

An additional note about the durability of this apparatus is the ability of the neck to be detached and resealed. When the apparatus is fully assembled, there is minimal access to the inside of the sphere, making it impossible to tighten the electrode nuts and/or clean the polycarbonate sphere. As mentioned, vacuum grease can splash on the walls of the sphere and it may be desirable to clean it off. The glue seal between the PVC sheet and the polycarbonate sphere can be cut rather easily with a knife edge or a pair of scissors. Once the PVC sheet is detached, the electrodes are accessible to be adjusted and the entire inside of the sphere can also be cleaned. Once all adjustments are made, the PVC sheet can be re-glued and the apparatus will be fully functional after the glue dries. The ability to cut away and reseal the glued component is an additional advantage over the glass.

3.7 Cost Analysis

In addition to the polycarbonate apparatus lasting much longer than the glass flask, it is also significantly cheaper. A cost analysis was conducted to compare the cost of a glass flask and a polycarbonate flask. Several components of the test apparatus are shared between the two, including the plumbing system, stirring system, electrodes and ignition system, and size 14 rubber stopper. These components were omitted from the cost comparison. The breakdown of costs to create each testing flask is shown in Table 3.5.

Table 3.5: Cost comparison of glass flask and polycarbonate flask.

Apparatus	Component	Supplier	Model #	Price
Glass	Pyrex 12 L Spherical Flask	Corning [25]	4260-12L	$235.80
			Total:	**$235.80**
Polycarbonate	30.5 cm Clear Smooth Polycarbonate Lighting Globe	Edith Aiken Company [19]	10012-CL-XX	$45.00
	PVC Unthreaded Pipe, 5.1 cm Diameter, 1.5 m long	McMaster-Carr [26]	48925K96	$9.60
	Type I PVC Sheet, 15.2 x 15.2 x 2.3 cm	McMaster-Carr [27]	8747K635	$5.65
	Dow Corning 700 Silicone Sealant, 3 oz.	McMaster-Carr [21]	7425A51	$4.35
	5.1 cm PVC Slip Flange[1]	PVC Fittings Online [28]	851-020	$5.70
	7.0 cm diameter brass rod[2]	Already present in lab	n/a	($73.00)[3]
			Total:	**$70.30**

[1] The PVC flange was cut to create the PVC ring that supported the sphere from the bottom.

[2] The brass piece was found in lab and cut down to specified weight. It was not purchased. Any material could be substituted for this weight.

[3] This is an estimated price for the brass [29]. Not incorporated into total cost for this polycarbonate prototype.

In summary, the polycarbonate flask is only $70.30 while the glass flask is $235.80. This does not account for the difference in longevity of each flask. The $235.80 glass flask becomes unusable after a small number of 2L refrigerant tests and must be replaced by a new one. Due to the extreme durability of the polycarbonate, and its ability to be resealed and cleaned, its value far surpasses the value of the glass flask.

3.8 Discussion and Recommended Changes

The polycarbonate apparatus was tested extensively and proved to be a better testing apparatus than the previously used glass flask. The polycarbonate assembly was constructed and sealed with a silicone sealant that did not leak through the entirety of the testing. The leak rate that was measured at vacuum pressure was well under the maximum allowable leak rate in ASTM E681. The polycarbonate also did not etch or show any loss of transparency after the testing. This is a significant improvement from the glass flasks which have a very short life span when testing refrigerants. A significant quenching effect from the electrode rods was quantified based on its effect on flame angle, and a solution was developed by inserting the electrodes through the side of the polycarbonate vessel. The PVC neck design allowed for a secure connection of the plumbing tree with a threaded fitting that did not need to penetrate through the rubber stopper. The weighted rubber stopper that was developed provided multiple benefits. The apparatus could consistently conduct tests at atmospheric pressure without leakage because of the

additional weight. Also, the additional weight ensured that the apparatus did not vent until after the flame had reached the wall. All of these benefits contributed to the reproduction of an accurate LFL of 14.6% (14.57 ± 0.07%) for R-32 at 101.3 kPa starting pressure, and an LFL of 14.8% (14.84 ± 0.09%) at 91.2 kPa starting pressure. The ability to produce an accurate LFL further solidifies that the polycarbonate apparatus is a suitable alternative to the glass flask. Additionally, a cost comparison shows that the polycarbonate flask is significantly cheaper than the glass flask. Finally, the lifespan of one polycarbonate flask shows to outlast several glass flasks, compounding the cost effectiveness of the polycarbonate.

It is recommended that ASHRAE 34 adopt a polycarbonate apparatus with the electrodes and other penetrations inserted from the side when testing the flammability limits of refrigerants and refrigerant blends. However, the apparatus that was designed for this research needs to be improved before a final design can be recommended for an updated test standard. Instead of the wooden platform, the polycarbonate sphere needs to be mounted inside of a testing enclosure to allow for testing at elevated temperatures. Also, the pulley system used to secure the weighted rubber stopper requires a person to hold the tether during testing. The final apparatus shall be fitted to secure the stopper without any help from a technician. Humidity was not addressed in this research because R-32 is not affected by it [23]. The final apparatus will need to have an added system that can humidify the air to a desired level.

It is also recommended that ASHRAE 34 require a 2.5 kg weighted stopper with no penetrations to be used instead of a rubber stopper with all of the plumbing

and electrodes penetrating through it. A standardized weight will ensure accurate test results by eliminating significant leakage at atmospheric pressure and ensuring the flask does not vent until after the flame reaches the wall. This will eliminate variability in venting conditions between laboratories and will help produce more consistent flammability limit results for refrigerants. In addition to the benefits from the weighted stopper, it is recommended that testings be conducted at a starting pressure of 91.2 kPa. The lower starting pressure has minimal affect on the reported LFL and helps to further ensure minimal leakage before ignition and full flame propagation before venting [6]. Also, some laboratory locations may have atmospheric pressures below 101.3 kPa, so having a standardized starting pressure of 91.2 kPa would be easier to achieve and provide added consistency between laboratories.

Chapter 4: Conclusions and Future Work

An alternative apparatus for ASTM E681 was constructed with a 30.5 cm diameter polycarbonate lighting globe and an attached PVC neck. Several components from a previously developed glass apparatus were modified for use with the polycarbonate apparatus. Lower flammability limit testing of R-32 at room temperature and starting pressures of 101.3 kPa and 91.2 kPa showed that the polycarbonate apparatus is a suitable replacement for the glass flask while providing several advantages. Three main problems with the test standard were identified and solved: the etching of the glass flask, the quenching of the flame by the electrode rods, and inconsistent venting and leakage caused by the several penetrations through the rubber stopper. The polycarbonate apparatus did not react with the HF from the combustion of refrigerants, creating no loss of transparency throughout testing. Also, the polycarbonate can be easily drilled through, allowing for the electrode rods to be inserted from the side and removed from the flame path. All penetrations were removed from the rubber stopper and an evenly distributed weight was added to the top. This prevented any leakage at atmospheric pressure and also ensured all venting occurred after the flame reached the wall. The apparatus was exposed to 60 °C for 45 minutes to show that its structural integrity will not be compromised if testing at that temperature.

This apparatus produced an accurate LFL for R-32 while adding several benefits to the test method. The reported LFL for R-32 is 14.8%, produced from tests at 91.2 kPa starting pressure. It is recommended that a polycarbonate apparatus of similar structure be incorporated into the test standard for determining the flammability limits of refrigerants.

Future work should focus on developing a refined polycarbonate prototype that can be directly implemented into the test standards for determining flammability limits of refrigerants. To do this, the polycarbonate apparatus must be mounted inside of the same steel and aluminum enclosure that houses the 12 L glass flask. This will remove all of the wood that was used to mount this polycarbonate prototype. A possible design for mounting the polycarbonate apparatus inside of the enclosure is shown in Figure 4.1. This figure shows the bottom plate with a hole for access to the magnetic stirrer. The plate is raised to support the polycarbonate sphere from the bottom. Once inside of the enclosure, testing can be conducted at 60°C. Alternative materials for the PVC neck should be investigated. Properties of PVC suggest that it might not withstand increased exposure to HF and high temperatures. A material such as polycarbonate may be a suitable replacement, given its proven durability throughout this testing. It may be desired to reduce the length of the neck to better match the neck from the 12 L glass flasks. This would require an alteration to the plumbing tree to avoid interference with the rubber stopper. Also, a humidity system must be incorporated that is capable of maintaining a consistent humidity level inside of the vessel.

After the polycarbonate apparatus is inside the oven, a solution shall be devel-

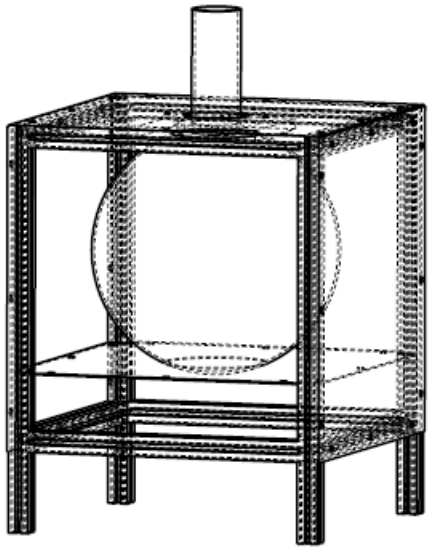


Figure 4.1: Proposed design for polycarbonate apparatus mounted inside of enclosure.

oped to safely secure the weighted rubber stopper after venting occurs. A suggested solution is to replace the brass weight with a similarly shaped steel weight, and use a mounted magnet to secure the weighted stopper after it lifts from the the neck during venting. This design is illustrated in Figure 4.2.

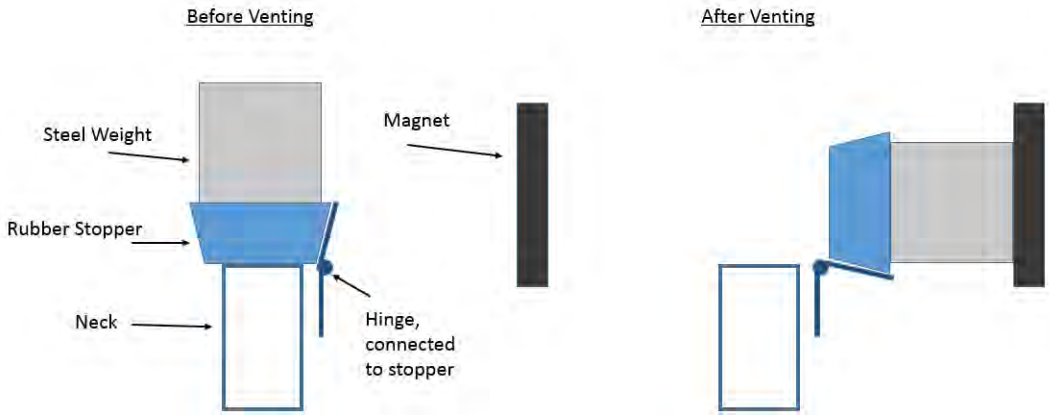


Figure 4.2: Proposed design for magnet to secure weighted rubber stopper after venting.

Appendix A: Additional Flame Angle Measurements

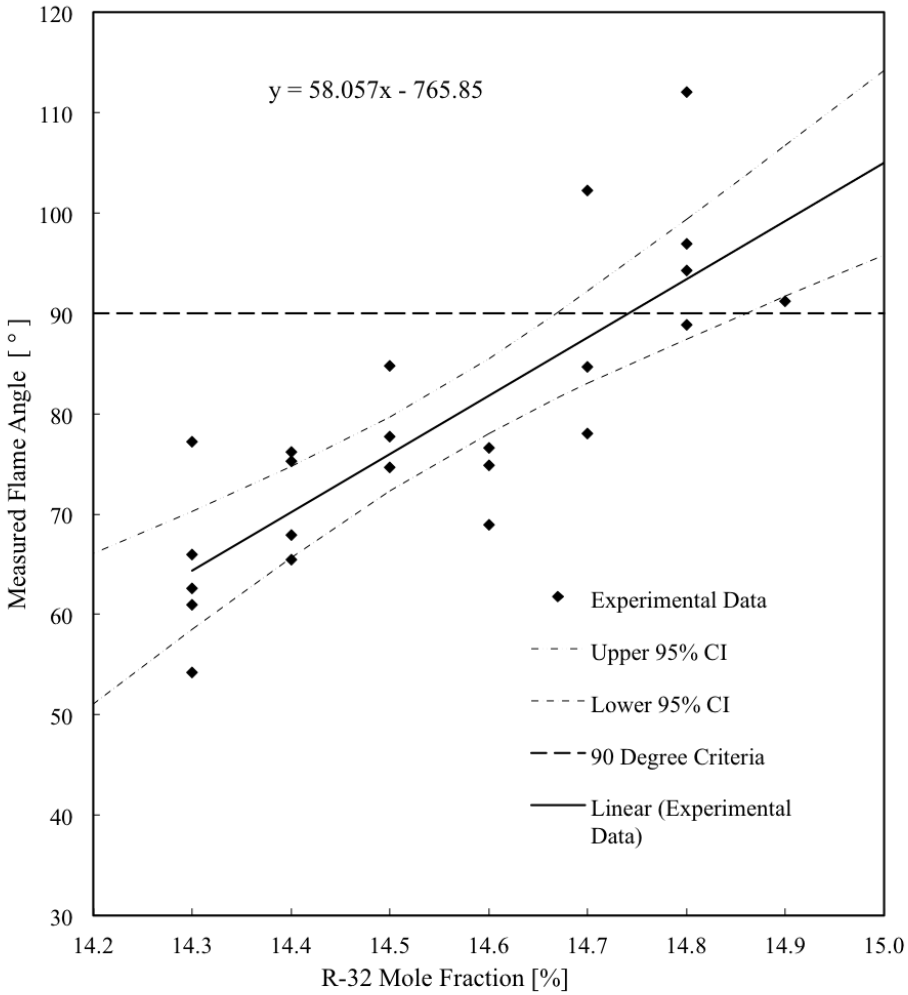


Figure A.1: Reproduced plot of measured flame angle vs. mole fraction of R-32, tested in glass flask by McCoy [4]. Yields LFL of 14.74 ± 0.12%.

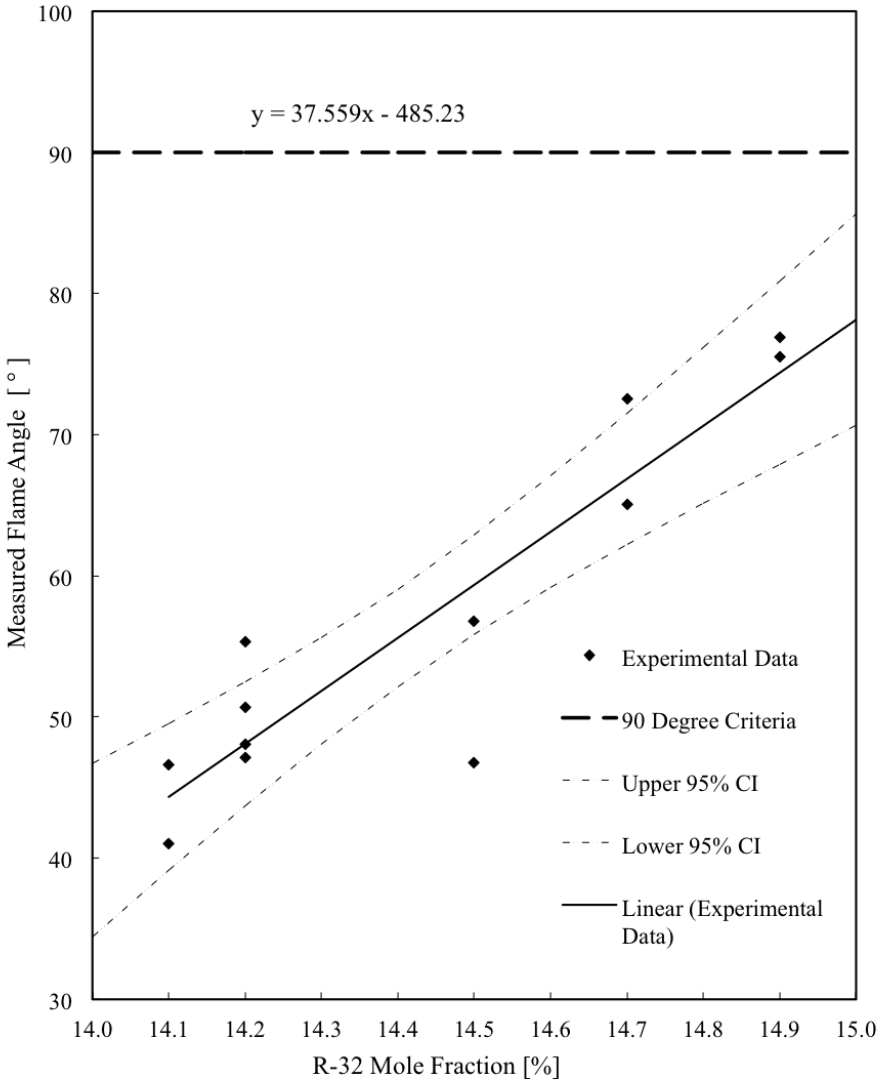


Figure A.2: Measured flame angle vs. mole fraction of R-32, produced in polycarbonate prototype at starting pressure of 81.1 kPa. Yields LFL of approximately 15.3% if linear best fit line is extended to intersect 90°. Limited tests conducted at 81.1 kPa prevented a confident determination of LFL.

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